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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report presents the results of completed and on-going research concerning the incineration and treatment of hazardous wastes. The information will inform those who own, operate, design, or regulate hazardous waste incineration and treatment facilities of current government-sponsored research in this area. For further information on this subject, interested parties should contact the Incineration Research Branch, Industrial Pollution Control Division, Industrial Environmental Research Laboratory, USEPA, Cincinnati, Ohio 45268.

David G. Stephan
Director
Industrial Environmental Research
  Laboratory
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PREFACE

These Proceedings are intended to disseminate up-to-date information on extramural research projects concerning land disposal, incineration, and treatment of hazardous waste. These projects are funded by the U.S. Environmental Protection Agency's Office of Research and Development and have been reviewed in accordance with the requirements of EPA's Peer and Administrative Review Control System.

ABSTRACT

The Eighth Annual Research Symposium on land disposal, incineration and treatment of hazardous wastes was held in Ft. Mitchell, Kentucky, on March 8, 9, and 10, 1982. The purposes of the symposium were (1) to provide a forum for a state-of-the-art review and discussion of ongoing and recently completed research projects dealing with land disposal, incineration, and treatment of hazardous wastes; (2) to bring together people concerned with hazardous waste management who can benefit from an exchange of ideas and information; and (3) to provide an arena for the peer review of the Solid and Hazardous Waste Research Division's and the Industrial Pollution Control Division's research programs in hazardous waste management. These Proceedings are a compilation of papers presented by the symposium speakers.

The symposium proceedings are being published as two separate documents. In this document, Incineration and Treatment of Hazardous Waste, six technical areas are covered. They are as follows:

(1) Hazardous Waste Incineration Overview
(2) Incineration of Hazardous Waste in High-Temperature Industrial Processes
(3) Laboratory and Pilot Scale Incineration Research and Development
(4) Incinerator Process Management
(5) Advanced Hazardous Waste Treatment and Control Technology
(6) Specialized Hazardous Waste Incineration Techniques

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1.0 INTRODUCTION

The purpose of this document is twofold: (1) to present information on the number, types, and capacities of hazardous waste incinerators put into operation since January 1969, and (2) to present information which analyzes and describes some of the more important design features of the various types of incinerators.

2.0 BACKGROUND

Prior to RCRA no major distinction was made between incinerators used for hazardous or nonhazardous wastes. They all had similar waste feed systems, burners, fans or blowers, closed comubstion chambers (nearly always lined with refractory materials), and stacks to disperse the flue gases. However, virtually every incinerator facility now in hazardous waste service in the United States should be equipped with at least one air pollution control device (APCD). The addition of APCDs does, of course, significantly add to incinerator capital cost requirements and operating expenses.

Within the past few years, the value of thermal energy has greatly appreciated, and thermal energy release from incinerators can be significant. Accordingly, this study has shown that almost 90 percent of all hazardous waste incinerator facilities ordered or placed into operation during the past year has been equipped with energy recovery systems.

3.0 TECHNICAL APPROACH

Most of the information collected for this study was obtained from one or more of the following sources:

a) Telephone conversations between a member of the MITRE technical staff and a responsible person at the vendors' offices.

b) Perusal of technical bulletins and literature furnished by most of the vendors.

c) Personal interviews by one or more of MITRE's technical staff with one or more of the vendors' staff at a mutually convenient location.

Initially, names, addresses and some telephone numbers of vendors were obtained from one or more listings in four current vendor directories, including:

a) 1981 Chemical Engineering Catalog

b) February 1981 Buyer's Guide, Solid Waste Management Magazine

c) 1981 Catalog and Buyer's Guide, Pollution Equipment News (Nov. 1980, Vol. 13, No. 6)

d) 1980-81 Directory and Resource Book, Air Pollution Control Association

Names of vendors not listed in the above directories were obtained from various other sources.

4.0 DATA PRESENTATION AND DISCUSSION

4.1 Types and Numbers of Incinerators

A breakdown of the statistical data obtained in this study on types and numbers of hazardous waste incinerators is presented in Tables 1, 2, and 3 on the following pages. Table 1.B shows a complete enumeration of hazardous waste incinerators by type and by the number of companies offering each type. In Table 2, there is a breakdown of the number of units of each principal type sold by the companies. Table 3 consists of individual listings of the 57 companies that market hazardous waste incinerators plus data pertaining to the types of incinerators that they market, the number, capacity, and wastes handled by each type in hazardous waste service, plus other details which were available on each company's product line or services. Table 3 occupies six pages, therefore only Page 1 of this table is presented in an abbreviated presentation.

A number of observations and conclusions can be drawn from analysis of the data in Tables 1, 2, and 3. Some of these are as follows:

o About 342 incinerators have been put into hazardous waste service since January 1969. These units were manufactured by 29 companies, all of which were based in the United States at the time the units were delivered. Within the past year one of these companies (BSP Envirotech) was purchased by a West German firm, the Lurgi Corporation. The count of 342 units is believed to be reasonably accurate but cannot be exact for the following reasons:

  a) A number of small vendor companies have disappeared since 1969. These companies have probably manufactured a few incinerators which are still in use but their existence could not be determined.

  b) Incinerators originally sold for hazardous waste disposal, or for non-hazardous wastes, could be operating, at least part-time, on the other waste.

  c) Some incinerators have been manufactured strictly in accordance with a customer's specifications and the manufacturing company has no knowledge of, or declines to speculate on, the nature of the purchaser's wastes.

  d) A few incinerators which have been manufactured since January 1969 are probably no longer in use. A vendor will not generally know this.

  e) A few incinerators manufactured since January 1969 cannot fulfill the design function and are not operating. Vendors will not voluntarily acknowledge them.

o The most common type of hazardous waste incinerator is liquid injection, representing 64.0 percent of all hazardous waste incinerators in service. This type of incinerator is not designed to operate on liquids containing any significant amount of salts or other suspended or dissolved solids.

o The next most common types of hazardous waste incinerators are the Fixed Hearth (F.H.) and the Rotary Kiln (R.K.), with 17.3 and 12.3 percent, respectively, of the total manufactured. Both of these types of units will dispose of solids and/or liquid wastes, plus fumes.

o Although there are nine companies offering Fluidized Bed (F.B.) incinerators, only nine such units are in hazardous waste service. Apparently most of these nine companies believe that the market is potentially good for this technology.

TABLE 1

SUMMARY DATA SHEET
HAZARDOUS WASTE INCINERATORS IN THE UNITED STATES

A. Number of Companies Offering Incinerators for Hazardous Waste Service:

Offering 1 Type Only	Offering 2 or More Types	Total No. Companies
45	12	57

B. Number of Hazardous Waste Incinerators in Service, by Type, and by Number of Companies Offering Each Type:

Type	No. Companies Offering	No. in Hazardous Waste Service	Percent of Total
Liquid Injection	23	219	64.0%
Fixed Hearth	12	59	17.3
Rotary Kiln	17	42*,†	12.3
Fluidized Bed	9	9	2.6
Multiple Hearth	2	7	2.0
Pulse Hearth	1	2	0.6
Rotary Hearth	1	2Δ	0.6
Salt Bath	2	0	...
Induction Heating	1	0	...
Reciprocating Grate	1	1Δ	0.3
Infrared Heating	1	1	0.3
Open Drum	1	0	...
Unknown	2	0	...
Total		342	100.0%

*Includes five R.K. units in construction

†Includes one oscillating kiln

ΔOne unit is in construction

TABLE 2

NUMBER OF COMPANIES SELLING HAZARDOUS WASTE INCINERATORS, BY TYPE

Number Units Sold Per Company	Incinerator Type				
	L.I.	F.H.	R.K.	F.B.	M.H.
Unk		2	1	1	
0	8		8	5	
1	3	1	3		1
2	2	2	2	2	
3	2	3	1		
5	1	1	1	1	
6	1				1
8	1		1		
10		1			
12		1			
17	1				
18		1			
19	1				
22	1				
54	1				
75	1				
Total No. Companies Selling Each Type Incinerator	23	12	17	9	2

Legend: L.I. - Liquid Injection
F.H. - Fixed Hearth
R.K. - Rotary Kiln
F.B. - Fluidized Bed
M.H. - Multihearth

TABLE 3

HAZARDOUS WASTE INCINERATOR VENDOR DATA
FOR THE UNITED STATES

Number	Company	Type Incinerator* Built	Units in HW Service in U.S.	Comments
1	Air Resources	L.I., followed by catalytic converter	1	Primarily in fume incin. business Supplies H.W. incins. only on request
2	Basic Environmental Engineering, Inc.	Pulse Hearth	2	Does not solicit H.W. business
3	Baumco, Inc.	L.I.	0	Primarily a burner vendor
4	Bayco Industries of California	Fixed hearth, Multi-chamber afterburner	≤12	
5	Bigelow-Liptak Corp.	L.I. R.K.	19 1	
6	Brule's C.E. & E., Inc.	L.I.	5	Also mfgs. fume incinerators

- Two companies are actively marketing Fused Salt Bath technology but there are no units in service or under construction yet.
- Of about 219 liquid injection units in service, about 129 (59%) were produced by two companies, John Zink and Trane Thermal. The data furnished by Zink are not well verified. Of 23 companies marketing L.I. incinerators, 8 have sold no units to date. However, several of the 8 indicate that sales are imminent.
- Of the 17 companies offering Rotary Kiln incinerators, 8 have sold none to date.
- Of the 9 companies offering Fluidized Bed incinerators, 5 have sold none to date.
- Of a total of 57 companies offering 14 types of incinerators, 28 have sold no units in the United States (several companies represent European technology, and all have sold at least one unit, each, in Europe).
- The fact that 28 (of the total of 57 companies) have not sold any units to date is indicative of the extent of (1) new technology being made available in the United States by both U.S. and foreign companies, (2) the formation of new corporate ventures in this field of technology, and (3) efforts by European companies to invade the U.S. market. It is therefore believed that the market, or technology, is not static at this point in time.
- Two companies are allegedly developing new technology, which they would not describe at this time. It is known that other companies are researching other techniques for hazardous waste incineration but these techniques are not described in this report. The new processes included plasma, microwave plasma, and several unusual fluidized bed techniques.

4.2 Capacities of Incinerators, by Type

Results of this portion of the study are summarized in Table 4. Sufficient data were obtained from the four predominant types of incinerators to show design capacity comparisons in terms of both pounds per hour and millions of Btus per hour. Results can be summarized as follows:

- The typical Fixed Hearth incinerator is the smallest of the four predominant types.
- The typical Liquid Injection and Rotary Kiln incinerators have about the same capacities.
- On the basis of a small amount of data, the typical fluidized bed incinerator is the largest of the predominant types.

The above summaries are based on a limited amount of data (incomplete population description), and therefore may not be highly accurate.

A few additional comments regarding incineratory capacity are worthwhile, as follows:

- The largest hazardous waste incinerator noted (a liquid injection unit) was rated at 150×10^6 Btu/hr, however vendors say that requests to quote on facilities as large as 300×10^6 Btu/hr are being received. Such facilities would have liquid injection or rotary kiln incinerators, or a combination of both feeding into a common afterburner. Fume incinerators or municipal waste incinerators as large as 300×10^6 Btu/hr presently exist.
- The one manufacturer of the rotary hearth incinerator states that a range of 3600-24,000 lb/hr is feasible for this design.

4.3 Some Important Incinerator Design Details

Design details investigated were, for the most part, those of greatest interest to an EPA or a state permit writer. These are as follows:

TABLE 4

Comparison of Design Capacity of Several Types of Hazardous Waste Incinerators

Type Incinerator	Typical Value Used	n*	Capacity, lb/hr	Typical Value Used	n*	Btu/hr x 10^6
Liquid Injection	Median	43	1,600	Median	50	8
Fixed Hearth	Average	48	810	Average	4	4.9
Rotary Kiln	Average	2	1,600	Median	34	10.3
Fluidized Bed	....	1	31,000	Average	5	45.5

* = Number of units for which capacity data were available. In some cases the same incinerators were used in both data sets (when mass and heat data were convertible).

- Operating temperatures, pressures, and residence times
- Incineration/combustion heat release rates
- Air requirements, including requirements in each combustion chamber when more than one chamber is used
- Refractories
- Burners; purchased or manufactured internally (the burners are so varied in design and range of function that a separate study could be justified on just this class of item)
- Instrumentation, controls and monitors (also too large a class to be handled in depth by this report)
- Heat recovery
- Trial burn facilities
- Air pollution control devices
- Vendors' scope of capability

4.3.1 Operating Temperatures, Pressures and Residence Times

Data obtained from 16 vendors of several types of incinerators are presented in Table 5. Since the data were obtained from small samples of rather small populations, they are not necessarily representative.

With respect to operating pressures, there is no wide range. Most incinerators operate a few inches w.c. (water column) on the positive or negative side of atmospheric pressure. The determining factor for the absolute pressure is the blower used. If a forced draft fan or blower is used to move combustion air and flue gases, then the combustion chamber will operate under a few inches of positive pressure. Negative pressures are encountered at installations with induced draft fans. "Push-pull" systems use both forced and induced draft fans and can operate under negative or positive pressures at various equipment locations. According to our sampling of the various populations:

- About half the vendors supply liquid injection incinerators which operate under slight vacuum, about half at slight positive pressure.
- All rotary kilns operate at slight vacuum.
- Fluidized bed incinerators require both forced draft and induced draft fans. The greatest pressure drop in the system is generally in the fluidized bed itself.
- Fixed hearth incinerators generally operate very close to atmospheric pressure (except in special cases), either on the positive or negative side.

Residence times in the several incinerator types vary considerably, especially in the Liquid Injection (L.I.) incinerators. One liquid injection incinerator vendor flatly specified 0.5 seconds gaseous residence time at 1800°F as an adequate condition for most wastes. However, most vendors design for two seconds or more. When solids are handled in rotary kilns, rotary hearths, or fixed hearths, solids residence times vary from 10 minutes to two hours; nevertheless, the volatile or evolved gases were always contained in an afterburner at a minimum temperature of 1600-1800°F for an average of two seconds.

4.3.2 Heat Release Rates

Heat release rates in the primary combustion chamber were available from only three vendors of entirely different types of incinerators. Surprisingly, the rates were quite similar, as is seen below:

Incinerator Type	Heat Release Rate Btu/hr-ft^3
Rotary Kiln	25,000-40,000
Fluidized Bed	20,000-35,000
Liquid Injection	25,000

It should be noted that both heat release rates and excess air use in any incinerator is largely a function of the state of the waste and its susceptibility to dispersion (i.e., viscosity in liquids particle size in solids).

4.3.3 Air Requirements

Requirements for combustion air vary widely; however, there is general agreement that the amount of excess air should be minimized if heat recovery is practiced. The following generalizations are made:

- Liquid injection incinerators always operate with an excess of air (20-60 percent in excess of stoichiometric air requirements), except when organic nitrogen containing compounds are burned. In this latter situation, an afterburner is used, the primary combustion chamber operates under starved air conditions and the secondary chamber operates with excess air.
- There is wide variation in air used in the operation of rotary kilns. Some kilns are operated in a starved air mode (50 to 100 percent of stoichiometric air); others are operated with up to 150 percent of excess air (250 percent of stoichiometric) in the kiln. Since rotary kilns are always operated with an oxidizing secondary combustion chamber (afterburner), the net result is an overall excess air usage (50-200 percent). Our data show that smaller rotary kilns (5-20 million Btu/hr) may operate under starved air conditions, but the larger units nearly always operate on excess air.
- The rotary hearth operates at pyrolytic conditions (almost no air present), but the follow-on fume incinerator operates with excess air, and a 2-4 percent oxygen content in the exhaust gas is desired.
- The one fluidized bed vendor that was interviewed quoted a 15 percent excess air usage in the bed. No fluidized bed incinerators that we have knowledge of operate with an afterburner.
- Fixed hearth incinerators commonly, but not universally, operate in a starved air mode (30 to 100 percent of stoichiometric air) in the first chamber. The afterburner always operates with operates with excess air, so that the overall excess air usage is about 30-100 percent.

4.3.4 Refractories

Of all design factors encountered in hazardous waste incinerators manufactured, the least consistent one appears to be the choice of refractory. Incinerator vendors state that they tailor the choice of refractory to the job requirement, and it is not possible to briefly summarize this design factor.

4.3.5 Burners

The industry, overall, seems to "split down the middle" with respect to make-or-buy decisions on burners. Liquid injection vendors are more apt to make their own burners (and to stress, in some cases, the advantageous operating characteristics of their burners), while rotary kiln vendors are more apt to buy burners, including the burners manufactured by the liquid injection vendors.

4.3.6 Instrumentation, Controls and Monitors

Little uniformity was found in the selection and placement of controls, instruments and monitors supplied by the vendors. The choice of instruments, etc. is generally dictated by the purchaser, who is influenced by local codes and federal regulations, by his own engineers, and possibly by a consultant. The philosophy of some users is to instrument and monitor as inexpensively and as sparsely as possible, while others virtually "go overboard," i.e., they instrument to obtain as much operating data as possible, using the finest equipment available.

Keeping in mind that a purchaser's specifications for instrumentation and monitoring are variable and do not necessarily constitute good engineering practice, the following generalizations are made:

- Shielded thermocouples are the temperature measuring device of choice. Two to four thermocouples are sometimes mounted in the combustion zone of an incinerator, and temperature differences exceeding prespecified limits between any two thermocouples can be cause for automatic shut-down or waste feed cut-off.
- Pressure monitoring taps are usually placed around incinerators,

TABLE 5

DESIGN OPERATING PARAMETERS
FOR SEVERAL TYPES OF
HAZARDOUS WASTE INCINERATORS

		Temp. $^\circ$F 1st Chamber	Temp. $^\circ$F 2nd Chamber	Absolute Pressure 1st Chamber Inches, W.C.	Residence Time 1st Chamber as Indicated	Residence Time 2nd Chamber Seconds
L.I.	Range	1800°-3000°	....	-4" to +10"	0.33-5.0 sec.	....
	Typical Value	2200°	....	-2" or +3"	2 sec.	....
R.K.	Range	500°-2300°	1600°-2800°	-.5" to -2.0"	....*	1.0-3.0
	Typical Value	1200°-1600°	2000°-2400°	-1.0"	$\leq$2 hr.	2.0
F.B.	Single Value	1350°	....	-1"	0.75-2.5 sec.	....
R.H.	Two Values	1000°-1600°	1800°-2800°	+0.05"	10-30 min.	2
F.H.	Two Values	600°-1600°	1200°-1800°	-.2" to +.2"	....*	$\sim$2.0

Legend: L.I. -- Liquid Injection
R.K. -- Rotary Kiln
F.B. -- Fluidized Bed
R.H. -- Rotary Hearth
F.H. -- Fixed Hearth
* -- Data not available

afterburners, quenches, scrubbers, other APCDs, fans and blowers, boilers, in stacks. Pressure drops (or rises) are monitored by differential manometer devices, and absolute pressures by manometers or various types of pressure gages. Instruments can be of either indicating or indicating/recording types. Unusual pressure drops across equipment items (especially the scrubbers) can actuate an automatic shut-down.

- Nearly all flame detectors are U.V. types. In smokey flames, flame rods are used to detect ionized gases, and in a few small units, thermocouple type flame sensors may be immediately next to a burner and a pilot flame. Although they are generally used to insure continuity of a flame, they are occasionally used to detect the presence of flame in undesirable locations. These detectors are used in all types of incinerators except fluidized beds (since there is no macroform of flame in these units). Flame detection is one of the primary bases for controls relating to automatic fuel and waste feed cutoff to burners and pilot lights.
- Monitoring of hot exhaust or cool stack gases for O_2, CO_2, CO, NO_x, SO_x, unburned hydrocarbons, HCl, and particulate matter is generally specified by the customer. The most frequently monitored gases are O_2, CO, and CO_2. Some of the other items are monitored once or twice per year. Most customers and vendors prefer monitoring of cooler stack gases, but a few prefer hot zone monitoring.

4.3.7 Heat Recovery

Thirteen hazardous waste incinerator vendors state that 65 to 100 percent of all recent inquiries for incineration facilities include heat recovery. The unweighted average is 87 percent. Several vendors automatically include heat recovery in any discussion with a prospective customer unless the customer specifically rules it out.

Several vendors have limits of incinerator capacity below which they feel the additional investment required for heat recovery will not have an adequate pay-off. However, there is little agreement on these lower limits. Some lower limits quoted are: 2, 4, and 7 million Btu/hr and 30 gal/hr (roughly equivalent to 2 million Btu/hr).

Most vendors think of heat recovery in terms of steam boilers, with steam pressures up to 250 psig. When an incinerator combustion chamber operates at 1800°F, any boiler should be able to generate steam at pressure of 150 to 250 psig, with boiler exhaust temperatures of 550°-600°F. These boilers are usually "water wall" type, have soot blowers, and tubes are non-finned. In a few cases heat recovery is used to produce hot water, to preheat process gases, to heat air for space heating, and to preheat combustion air.

Most vendors quote on water-wall boilers, but one vendor prefers fire-tube boilers and another vendor specified fire-tube boilers when HCl was present to any significant extent in the hot exhaust gases. However, fire-tube boilers are rarely constructed to exceed 15 x 10^6 Btu/hr capacity.

The presence of significant amounts of alkaline salts (Na, K, Ca) and heavy metals will tend to depress the incinerator heat release rate. Further, the detrimental effects of the resulting particulates will triple the price of a waste heat boiler.

4.3.8 Trial Burn Facilities

Of 15 vendors, 11 have trial burn units available, and two vendors will attempt to lease a full-scale unit from a prior customer for trial burn purposes. Two liquid injection vendors claim that trial burns are not required and that the proper laboratory data will suffice to insure an adequate incinerator design. The range in capacity of the above trial burn units is from 150,000 to 3 x 10^6 Btu/hr. Several of these units represent the smallest model of incinerator available from the vendor.

4.3.9 Air Pollution Control Devices

The selection of the proper air pollution control device (APCD) is dependent on a number of factors, including:

- Federal regulations regarding emissions
- Properties of the wastes burned
- Type of incinerator used
- Local codes in the areas where the facility is to be installed
- Customers' preferences
- Costs (capital and operating)

At least one APCD is required with most incinerators, but a number of installations (especially commercial incinerators) require two devices, in series with each other.

It is not within the scope of this study to describe the construction or mode of operation of APCDs in any detail. The principle APCDs now in use include the following:

- Venturi scrubber
- Packed tower scrubber
- Sieve tray scrubber
- Spray tower scrubber
- Ionizing wet scrubber
- Bag house (bag filter)
- Cyclone
- Electrostatic precipitator (ESP)
- Wet ESP

The most commonly used devices include the venturi and the packed tower scrubbers. The former is particularly effective with high particulate loadings in the exhaust gases, and the latter is particularly effective in removing soluble acid gases providing the particulate loading is low. Bag houses have temperature limitations and do nothing to undesirable gases. ESPs are very effective for particulate removal but have a high capital cost. Ionizing wet scrubbers and wet ESP are also costly but are gaining in popularity.

APCDs are positioned downstream from any energy recovery device, and frequently require installation of a quench chamber to cool the polluted gases to a point where thermal damage will not occur to the APCD, or to prevent excessive evaporation of water in the APCD.

In prior years, venturi or packed tower scrubbers were made of carbon steel, stainless steel, or other alloys, depending on the acidity and corrosivity of the gases. However, in recent years these devices have been manufactured using Fiber Reinforced Plastic (FRP) or rubber-lined steel, and this construction is now very popular.

Of 16 vendors contacted, 15 prefer venturi and/or packed tower scrubbers, and one vendor (for rotary hearths) says none is needed for his unit.

4.3.10 Capability to Provide Services

Sixteen incinerator vendors (including one vendor who produces two types of incinerators) were queried regarding their capabilities for furnishing services on incinerator installations past the incinerator design and manufacturing stage. The following spectrum of responses was obtained:

- Design and manufacturer only
- Design and manufacture only but refractories set in place in field installations
- Design, manufacture and install
- Design through start-up but no site development
- Design through start-up
- "Turnkey"
- "Turnkey" plus contract operation and/or maintenance

For purposes of this report, a turnkey contract is defined as a fixed price contract in which a vendor agrees to design and furnish a completely erected plant, and will turn the facility over to a client wholly operable and debugged, often including performance guarantees.

A study of the above data does not reveal any trend or prevalent scope of capability. Many small units, and particularly the fixed hearth incinerators, are frequently supplied as skid-mounted, package units. Larger incinerators require field erection. Installation costs are generally much less for the package units. Nearly every vendor desires to attend or participate in any facility start-up where his equipment is involved, even if he is not primarily responsibile for start-up.

HAZARDOUS WASTE INCINERATION COSTS

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ABSTRACT

This paper describes the development of a method to estimate the capital and direct operating costs associated with hazardous waste incineration. The structure of the cost estimating method is described and the factors affecting incineration costs are listed. Cost estimates developed using this method will provide a basis for the financial analysis of incineration included a part of the Regulatory Impact Analysis for the Interim Final Incinerator Standards.

INTRODUCTION

The purpose of this study is to provide EPA with a method to estimate the capital and operating costs associated with hazardous waste incineration. Cost estimates developed using the information obtained from this study will provide a basis for the financial analyses included as part of the Regulatory Impact Analysis for the Interim Final Incinerator Standards.

The cost analysis developed during this study may be used to obtain budget estimates of the capital and operating costs for other purposes as well. Such estimates may be used by industry and government agencies to evaluate the costs of waste disposal options. The report developed from this study is intended to fill the information gap between engineers highly skilled in the design and technology of hazardous waste incinerators and those people having an interest, but not extensive experience, in this field.

Hazardous waste incinerator facility designs and costs vary considerably. There are 57 companies presently marketing incinerators that may be used for hazardous waste destruction. Probably no two incinerator designs developed by these manufacturers are identical. There is no 'typical' incinerator design or facility. Recognizing this fact, this method for cost estimation is designed to address the many different incinerator facility designs found within the industry. The versatility is attained by identifying the major components of an incinerator facility and providing estimates of the cost of each component. The appropriate components may be selected and a cost estimate developed for a particular facility as each situation warrants.

The costs developed from this study represent averages derived from a limited sampling of approximately 25 incinerator component manufacturers, and the owners and operators of hazardous waste incinerators. The costs provided by manufacturers are budget estimates, accurate to within twenty percent of actual costs. In order to develop more accurate cost figures, detailed design specifications must be provided and considerable engineering must be conducted. A price quote for a complete incinerator facility generally requires about twelve man weeks to prepare and may require as many as thirty man weeks. The use of the predictive model developed during this study will produce a cost estimate in hours.

The use of average costs suffers a limitation in that quotations developed by different vendors to the same specifications often vary considerably. The highest bid for an incinerator facility may be more than twice that of the lowest. The variations in quoted prices are the result of different approaches to design, inclusion of auxiliary equipment, and different methods of construction. The competitiveness of the incinerator market also influences prices, some vendors submit low bids in order to establish a market.

Factors Affecting Incineration Costs

The factors affecting the cost of hazardous waste incineration are grouped into three broad categories:

- Waste characteristics
- Facility characteristics
- Operating characteristics

The specific factors incorporated in the cost estimating method are listed in Figure 1. The major factor affecting equipment costs is the heat input rate to the incinerator. Accordingly, costs are presented graphically as a function of equipment size, expressed as heat input rate or flue gas volume flow rate. The other factors are expressed as multipliers that are applied to the values obtained from the graphs.

In order to obtain reasonably accurate cost estimates, the incinerator facility components must be properly sized. Equipment sizes and the auxiliary fuel requirement are obtained from an elementary heat balance presented in the report. The heat input from the waste is subtracted from the sum of energy losses from the incinerator, including flue gas enthalpy, water vapor enthalpy, and radiation losses. If the energy loss exceeds the heat input, the difference must be made up through the use of auxiliary fuel. The flue gas enthalpy and water vapor enthalpy are determined graphically, and a sample calculation is shown in Figure 2.

The flue gas volume is a function of the incinerator heat input and excess air usage. Flue gas enthalpy is a function of combustion zone temperature and flue gas volume. In this example, energy losses exceed the heat input rate by 4.8 million Btu and the dotted line indicates the flue gas volume using auxiliary fuel to compensate for the loss.

Not all the heat content of auxiliary fuel can be utilized because of associated combustion gas enthalpy loss. The enthalpy loss is a function of the combustion zone temperature. In Figure 3, the effects of enthalpy loss expressed as the combustion zone temperature on the costs of three auxiliary fuels are shown. It is much more expensive to use #2 fuel oil as an auxiliary fuel than to use natural gas.

Incinerator Facility Costs

Graphs showing equipment cost as a function of size are presented in Figures 4, 5, and 6. The costs of the three major types of hazardous waste incinerator facilities include air pollution control equipment, energy recovery equipment, a waste storage and loading system, and the combustion chambers. The capital cost of an installed incineration facility is approximately 1.5 times the freight on board (FOB) costs obtained from the graphs. It should be noted that the costs of liquid injection and hearth incineration facilities of the same heat input are approximately three times as expensive. The high cost of the rotary kilns is offset by their ability to incinerate all types of wastes.

More detailed estimates can be developed using the graphs for each of the major components of an incinerator facility that are included in the report. Capital cost information is presented for ram loaders, combustion chambers, energy recovery equipment, and air pollution control equipment. Incinerator facility installation, start-up, spare parts, engineering, control and instrumentation costs are estimated as percentages of the total equipment cost.

Annual direct operating costs are estimated using information included in the report for each of the following expenses:

- Labor
- Utilities and chemicals
- Incinerator effluent management
- Maintenance
- Laboratory analyses

Methods to estimate usage and rates are presented for each of these functions except for maintenance costs, which are estimated as a percentage of the total capital cost. Guidelines for selecting typical operating conditions, including water flow rates, electrical power consumption and chemical usage, are provided. Steam generated by energy recovery equipment is applied as a credit to the incinerator operating cost.

The total capital cost can be depreciated on a straight line basis and added to the annual operating cost estimate to give an estimate of the total annual cost of incineration. Such estimates may be used to compare the effects of varying incinerator operating conditions, such as combustion zone temperature and residence time, and the numerous incinerator design alternatives on the total cost of hazardous waste incineration. In addition, financial analyses may be conducted, using the information from this economic analysis, to determine the costs of incineration under various incinerator designs, operating conditions, regulatory requirements, and market-place conditions. Such a financial analysis would incorporate the cost of money and revenues from hazardous waste management into the cost of hazardous waste incineration.

- Waste Characteristics
  - Physical state
  - Heating value
  - Water content
  - Organic chloride content
  - Alkali metal content
  - Container size

- Facility Characteristics
  - Waste storage capacity
  - Incinerator type
  - Energy recovery
  - Materials of construction

- Operating Characteristics
  - Waste input rate
  - Operating schedule
  - Combustion zone temperature
  - Combustion zone residence time
  - Excess air usage

Figure 1

Factors Affecting Hazardous
Waste Incineration Costs

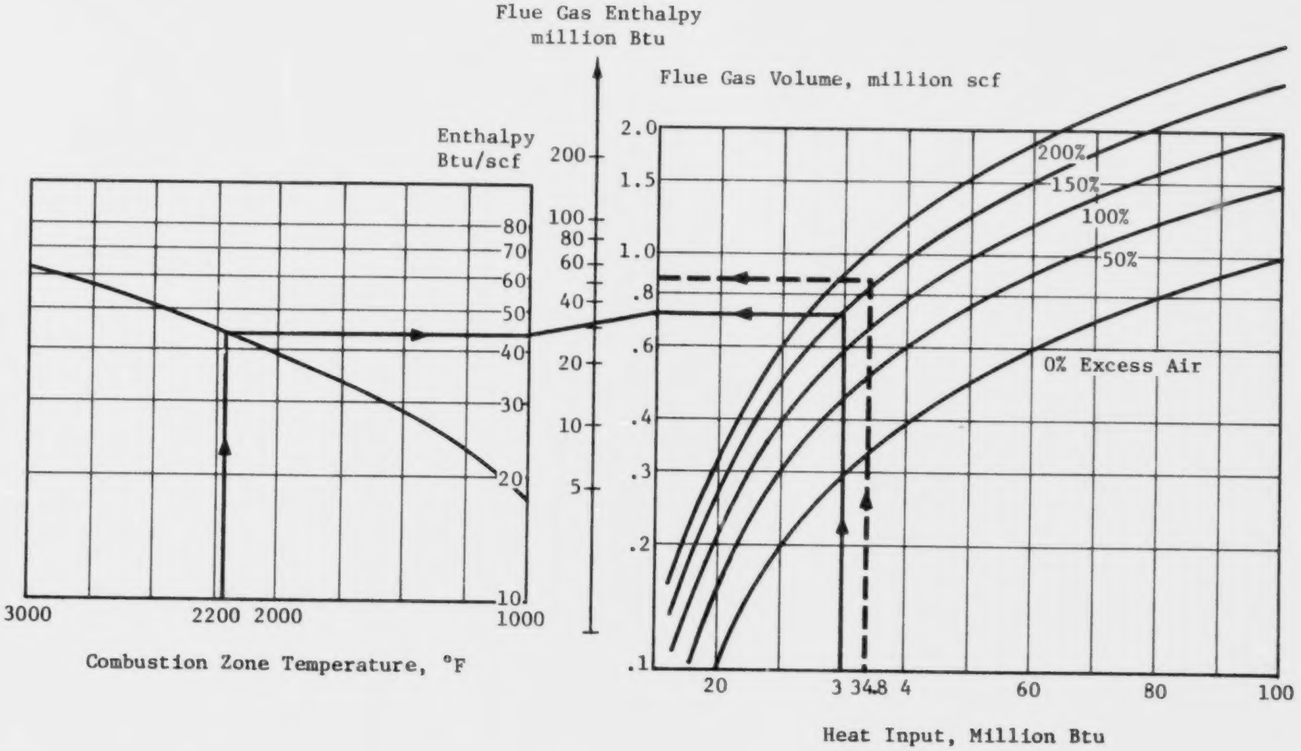
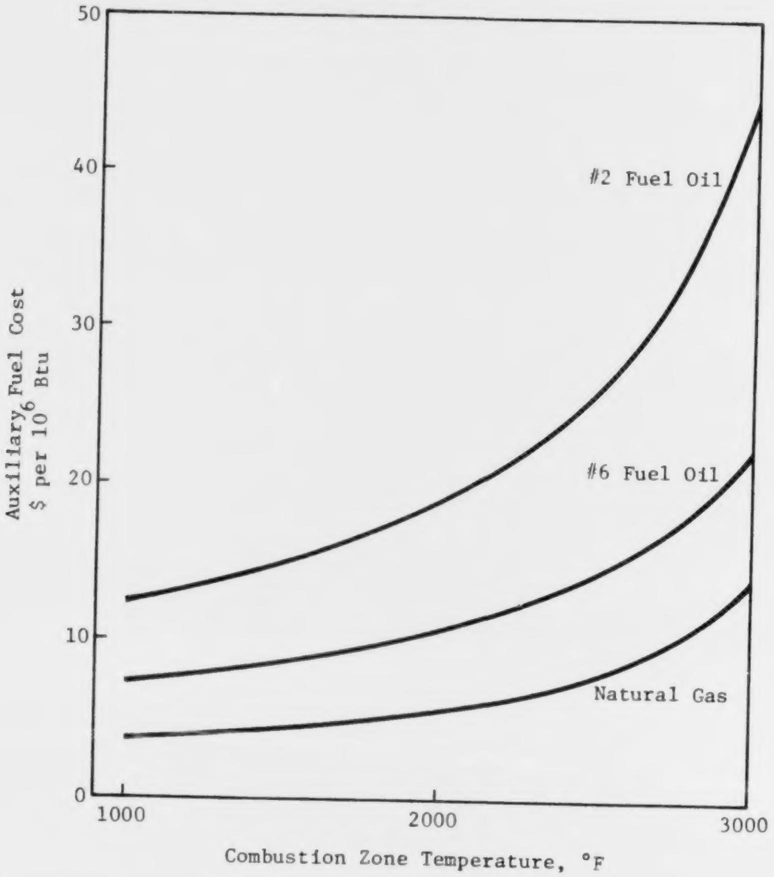


FIGURE 2

CALCULATION OF FLUE GAS VOLUME AND ENTHALPY



Basis: Stoichiometric combustion of fuels

	March 1981 Price	Heat Content
#2 Fuel Oil	$1.25 per gallon	137,000 Btu/gal
#6 Fuel	$ .86 per gallon	153,000 Btu/gal
Natural Gas	$2.69 per 1000 scf	1020 Btu/scf

FIGURE 3

AUXILIARY FUEL COST AS A FUNCTION OF TEMPERATURE
(DERIVED FROM AVAILABLE HEAT CALCULATIONS)

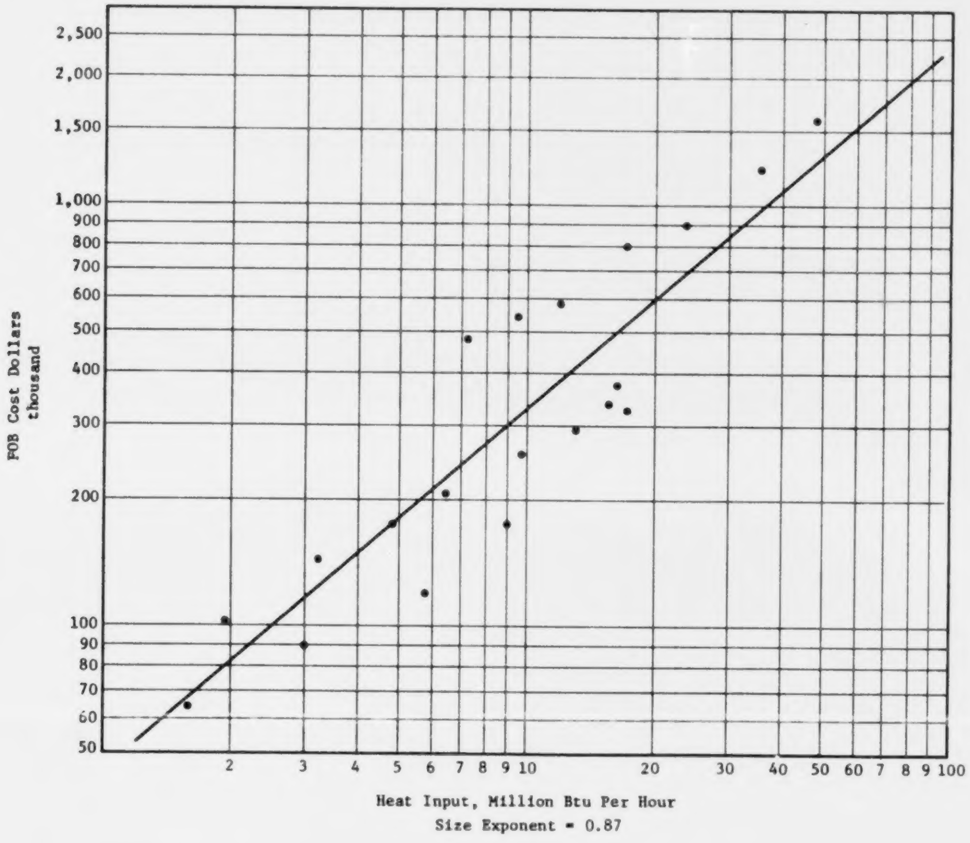


FIGURE 4

HEARTH INCINERATOR FACILITY COST AS A
FUNCTION OF HEAT INPUT

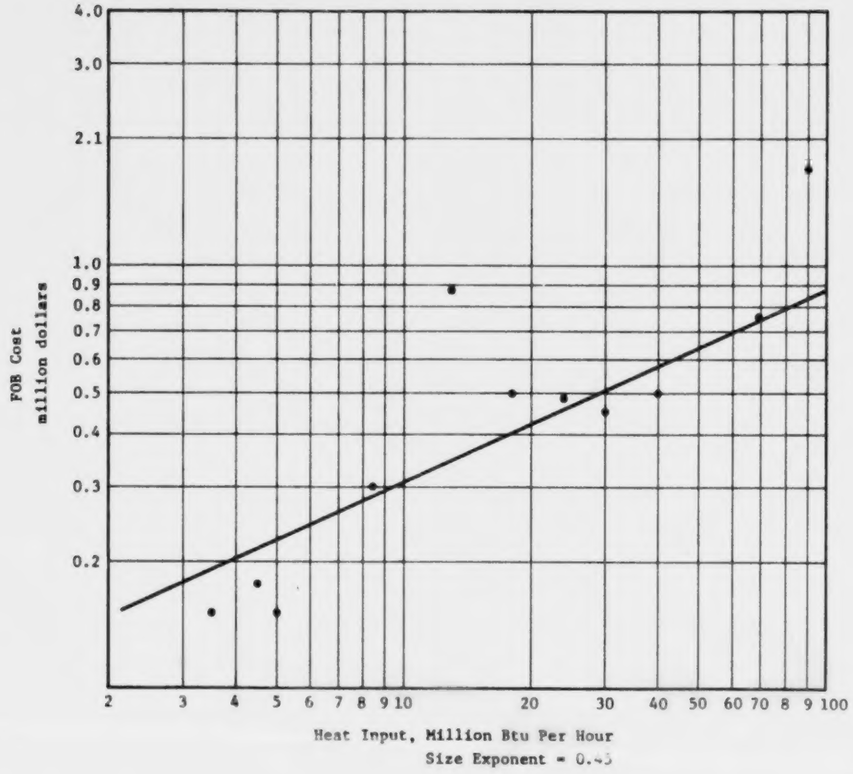


FIGURE 5

LIQUID INJECTION INCINERATOR FACILITY COST

AS A FUNCTION OF HEAT INPUT

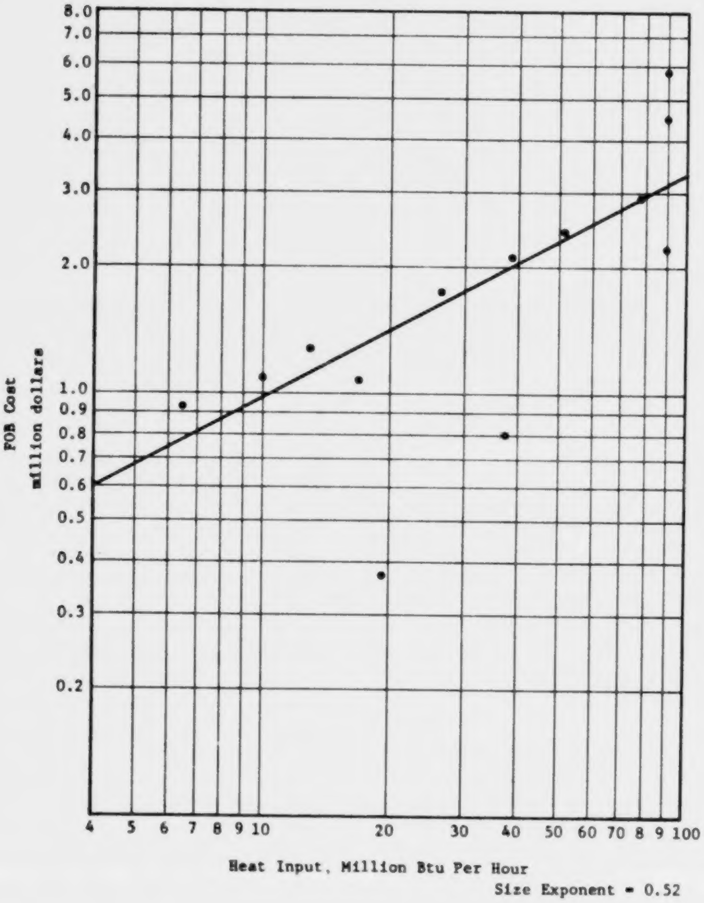


FIGURE 6

ROTARY KILN INCINERATOR FACILITY COST AS
A FUNCTION OF HEAT INPUT

USING UNCERTAINTY ANALYSIS TO ESTIMATE THE COST OF HAZARDOUS WASTE INCINERATION

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ABSTRACT

This paper presents the rationale for, and the result of using uncertainty analysis or probabilistic simulation to estimate the cost of hazardous waste incineration. Results are presented giving the probability distributions for capital cost and the present value of average net costs over the life of a rotary kiln for PCB wastes.

INTRODUCTION

A major technology for the destruction of hazardous wastes is incineration, for which there are a number of candidate technologies available, some proven, some not. The proven technologies are rotary kilns and liquid injection incinerators. The technologies that are still largely experimental are fluidized beds, molten salt and co-incineration.

Even for the proven technologies, however, there is much uncertainty regarding the costs of incinerating the various wastes thought appropriate for kilns and liquid injection. This uncertainty arises from three principal characteristics: variations in waste types, facility design and economic factors. There is a wide variety of waste types that require different operating conditions and input combinations, such as excess air, supplementary fuel, neutralizing agents, etc. Variability in design characteristics stem from such factors as variations in air pollution control equipment and in heat recovery technologies. The third major source of uncertainty stems from variations in economic parameters such as interest rates, fuel prices, steam prices, wage rates, etc.

These variabilities have always presented a problem to the cost analyst; the usual procedure adopted to deal with the problem has been to choose the "best" estimate (a mean or judgmental figure) of parameters, often consciously erring on the conservative side (overestimating costs, underestimating revenues). In addition, analysts often state that the final figure of interest (i.e. average cost, total cost, etc.) may vary by a factor of, e.g., ± 20%. This latter statement usually bears only a vague resemblance to the actual underlying variabilities, and as a result such *ad hoc* procedures do not have much meaning in a probabilistic sense. Even if the ±20% figure were interpreted in the context of a standardized normal distribution, it would typically involve an unwarranted inference about the variance of the estimate because the variance was not estimated directly.

In the light of these observations, one can see that cost estimation is a complex task even if done with the best of historical data - it becomes precarious with new and emerging technologies. The technique described above, denoted here as the traditional approach, being essentially *ad hoc* in nature, does not fully nor effectively exploit the information possessed by an analyst or the experts on which he may rely regarding the variability of component performance characteristics and costs. This technique essentially throws away information about underlying variabilities or probability distributions.

Neither does the traditional approach allow decision makers to know the margin of error present when choosing a given cost figure to represent the "best" estimate to be used in policy making. In particular, in an environment that heavily penalizes excessive costs, it is important for the decision-maker to know the probability that a given cost figure will be exceeded, information that the traditional approach does not provide. From the viewpoint of environmental regulation, decision makers need to know the probability attached to the cost of meeting a standard, so that cost trade-offs can be analyzed explicitly. From the viewpoint of the regulated firm, it is important to know the distribution of costs for meeting a standard, since this affects profit.

This paper reports on the application of uncertainty analysis to the problem of estimating the cost of hazardous waste incineration. The technique is variously known as model sampling, stochastic simulation or Monte Carlo analysis. The technique is straightforward, and requires only that the cost model be written down as a set of equations, and that all variables and parameters deemed to be uncertain be written as probability distributions (either classical or empirical). EPA staff have prepared a computer simulation program which conducts the model sampling - the output is a probability distribution for the variable of interest, as well as a number of other associated outputs.*

APPLICATION TO HAZARDOUS WASTE INCINERATION

The technique was applied to model of technologies for hazardous waste incineration, rotary kiln and liquid injection, for five wastes: polychlorinated biphenyls, nitrochlorobenzene, polyvinyl chloride, ethylene glycol and methyl methacrylate. The engineering model on which the cost estimates were based was a fairly modest one, in that it does not detail the basic unit processes such as waste storage, loading systems, combustion chambers, energy recovery equipment, etc. Capital items were dichotomized into only the basic furnace plus the air pollution control system, and the basic inputs determining operating costs were fuel, water, maintenance, neutralizing lime, electricity and labor. Only lime, supplementary fuel and the feed rate varied as the waste type changed. For the analysis, 15 variables and parameters were deemed to be uncertain enough to require probability distributions instead of point estimates as input data - in all cases, these were chosen as empirical distributions. As an example, this distribution was chosen for the electricity cost growth rate:

Probability	Rate
0.10	0.06
0.20	0.07
0.40	0.08
0.20	0.09
0.10	0.10

For most cost studies, it will likely be true in general that the distributions for economic parameters will have to be chosen as empirical distributions; the engineering parameters will be more amenable to the use of parametric probability distributions.

The procedure is straightforward - the computer is instructed to make repeated calculations of the model outputs choosing randomly from the 15 probability distributions for each iteration (1000 iterations is usually sufficient).

For the present case study, the model was programmed to yield the following outputs:

1. probability distribution for capital cost (furnace plus air pollution control equipment).

2. probability distribution of the present value of average cost (defined as the cost per ton of waste incinerated over the life of the facility).

3. average net operating costs in each of the years of operation.

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*The simulation routine is named "MOUSE"; copies of the program description and a tape of the program may be obtained by contacting the author or Dr. Albert J. Klee, Senior Science Advisor, IERL, U.S. EPA, Cincinnati, Ohio 45268, (513 684-4319).

Two basic types of cost estimates were sought: (1) financial cost or engineering cost estimates and (2) economic cost estimates. Financial costs include interest payments and taxes not paid for a specific governmental service, whereas the economic costs do not include those. Financial costs are those of most interest to the owners and users of facilities, as they relate to current profits and budgets, whereas the economic costs focus on the opportunity costs of incineration, that is the value of resources actually employed in the facility. It is these latter costs that give the policy-maker a clue to the true economic burden that hazardous waste incineration places on the economy.

Finally, the following 15 variables were estimated as empirical probability distributions for the kiln model: kiln capital cost, kiln installation cost, air pollution control capital cost, air pollution control installation cost, facility life, discount rate, capacity utilization, labor cost growth rate, electricity cost, electricity cost growth rate, water price, water price growth rate, steam price, steam/price growth rate, and fuel price growth rate.

THE COST ESTIMATES

Tables 1-3 give the estimates of the financial costs for incinerating PCB's in a rotary kiln. Table 1 shows the distribution for the capital items (furnace plus air pollution control). The mean estimate is $13.3 million, with a standard deviation of $0.95 million. Of more interest is the range ($12 mm to $16.3 mm), and the probability distribution of costs. In particular, one can see that the cummulative probability associated with the mean estimate is somewhat less than 65% - that is, there is a 65% probability that the capital cost will be $13.3 mm or less, and a 35% probability that it will be greater.

Table 2 gives the present value of the net average financial cost of incinerating one ton of PCB waste over the life of the facility (17 years here). The figure shown is the cost net of steam revenues from the heat recovery operation. The mean net cost of $87/ton occurs with a cummulative probability of 62%, and there is a 38% probability that the cost will exceed this figure. There is, however, only a 5% probability that the net cost will exceed $110/ton.

Table 3 gives the present value of the net average economic (as opposed to financial) cost for the kiln. This is significantly lower than the financial cost figure ($32/ton vs. $81/ton), the difference being solely that the economic costs exclude interest payments on debt, and financial cost figures include them. Thus, the true economic cost is substantially less than the financial cost, and furthermore, the two cost distributions do not overlap at all. As mentioned earlier, the financial cost figures are relevant to facility owners and their customers, and the economic cost estimates are relevant to environmental policy makers who need to gage the total economic burden environmental regulation places on the economy.

An additional output for which the model was programmed was the annual average net operating cost in each year of the facility life, 17 years in this case. Table 4 shows these figures for the financial cost model. The output shows that beginning in the seventh year of operation, the process yields a negative cost, or a net operating profit. The economic operating cost estimates for this model are the same, as the financial and economic cost models differ only in the treatment of interest payments.

Finally, although one may readily agree that having the probability distributions of costs represents a valuable addition to available information, there is the issue of whether or not the cost of uncertainty analysis is so high as to exceed the perceived benefits. Actually, there is some uncertainty about the cost of using uncertainty analysis, so a stochastic simulation was performed on that question. A model was constructed using the following variables, with uniform distributions employed as the probability distributions (ranges appear in parentheses: computer run time (3 to 6 minutes), number of runs (10 to 15), labor cost ($8.93 to $15.41 per hour), number of labor hours (40 to 60), cost per run at

TABLE 1. ROTARY KILN CAPITAL COST

```
                          **************************************************
                          *          MOUSE VERSION 2.0 JULY 1981           *
                          * (MODULAR ORIENTED UNCERTAINTY SYSTEM EMULATOR) *
                          *           WRITTEN BY ALBERT J. KLEE            *
                          **************************************************


NUMBER OF ITERATIONS =   300          MEAN =  13428686.00000                STANDARD DEVIATION =    975146.50000
                                   MINIMUM =  11993519.00000          COEFFICIENT OF VARIATION, % =         7.26167
                                   MAXIMUM =  16043279.00000


        LOWER  NUMBER OF   PERCENT  CUMULATIVE  CUMULATIVE                         DISTRIBUTIONS
        LIMIT    ENTRIES   ENTRIES   % ENTRIES  COMPLEMENT     * = FREQUENCY DISTRIBUTION     0 = CUMULATIVE FREQUENCY DISTRIBUTION

11940684.0000         3.      1.00        1.00       99.00     *0******
12064212.0000        11.      3.67        4.67       95.33     ***0************************
12187740.0000        18.      6.00       10.67       89.33     *******0************************************
12311268.0000        14.      4.67       15.33       84.67     ***********0***********************
12434796.0000        29.      9.67       25.00       75.00     ******************0****************************************************
12558324.0000         9.      3.00       28.00       72.00     ********************0**
12681852.0000         8.      2.67       30.67       69.33     ******************** 0
12805380.0000        15.      5.00       35.67       64.33     *************************0***********
12928908.0000        13.      4.33       40.00       60.00     ****************************0***
13052436.0000        18.      6.00       46.00       54.00     ********************************0***********
13175964.0000        17.      5.67       51.67       48.33     ************************************0*****
13299492.0000        13.      4.33       56.00       44.00     ********************************       0
13423020.0000        27.      9.00       65.00       35.00     **********************************************0*******************
13546548.0000         8.      2.67       67.67       32.33     ********************                           0
13670076.0000         5.      1.67       69.33       30.67     *************                                    0
13793604.0000         5.      1.67       71.00       29.00     *************                                     0
13917132.0000         5.      1.67       72.67       27.33     *************                                      0
14040660.0000        11.      3.67       76.33       23.67     ****************************                         0
14164188.0000         9.      3.00       79.33       20.67     ***********************                                 0
14287716.0000         8.      2.67       82.00       18.00     ********************                                     0
14411244.0000         6.      2.00       84.00       16.00     ***************                                            0
14534772.0000         4.      1.33       85.33       14.67     ***********                                                 0
14658300.0000         8.      2.67       88.00       12.00     ********************                                          0
14781828.0000         1.      0.33       88.33       11.67     ***                                                           0
14905356.0000         6.      2.00       90.33        9.67     ***************                                                0
15028884.0000         5.      1.67       92.00        8.00     *************                                                   0
15152412.0000         7.      2.33       94.33        5.67     ******************                                                0
15275940.0000         5.      1.67       96.00        4.00     *************                                                      0
15399468.0000         6.      2.00       98.00        2.00     ***************                                                      0
15522996.0000         4.      1.33       99.33        0.67     ***********                                                           0
15646524.0000         0.      0.00       99.33        0.67     *                                                                     0
15770052.0000         0.      0.00       99.33        0.67     *                                                                     0
15893580.0000         1.      0.33       99.67        0.33     ***                                                                   0
     OVERFLOW         1.      0.33      100.00        0.00     ***                                                                   0
```

TABLE 2. NET AVERAGE FINANCIAL COST-PCB WASTES

```
NUMBER OF ITERATIONS =   300         MEAN =       87.47615              STANDARD DEVIATION =        13.33162
                                  MINIMUM =       55.94403        COEFFICIENT OF VARIATION, % =   15.24029
                                  MAXIMUM =      126.67773

       LOWER   NUMBER OF    PERCENT  CUMULATIVE  CUMULATIVE                        DISTRIBUTIONS
       LIMIT     ENTRIES    ENTRIES   % ENTRIES  COMPLEMENT    * = FREQUENCY DISTRIBUTION     O = CUMULATIVE FREQUENCY DISTRIBUTION
     54.2687          1.       0.33       0.33       99.67    O**
     56.6138          1.       0.33       0.67       99.33    O**
     58.9579          0.       0.00       0.67       99.33    O
     61.3019          2.       0.67       1.33       98.67    *O****
     63.6460          6.       2.00       3.33       96.67    **O************
     65.9901          8.       2.67       6.00       94.00    ****O***************
     68.3342          6.       2.00       8.00       92.00    ******O********
     70.6783          8.       2.67      10.67       89.33    *******O************
     73.0224         15.       5.00      15.67       84.33    ***********O*************************
     75.3665         20.       6.67      22.33       77.67    ****************O********************************
     77.7105         23.       7.67      30.00       70.00    *********************O***********************************
     80.0546         29.       9.67      39.67       60.33    ****************************O******************************************
     82.3987         23.       7.67      47.33       52.67    *********************************O***********************
     84.7428         24.       8.00      55.33       44.67    ***************************************O*******************
     87.0869         21.       7.00      62.33       37.67    ********************************************O*******
     89.4310         23.       7.67      70.00       30.00    *************************************************O*******
     91.7751          6.       2.00      72.00       28.00    ***************                                   O
     94.1191         16.       5.33      77.33       22.67    ****************************************              O
     96.4632         13.       4.33      81.67       18.33    ********************************                         O
     98.8073          9.       3.00      84.67       15.33    ***********************                                    O
    101.1514         10.       3.33      88.00       12.00    *************************                                     O
    103.4955          7.       2.33      90.33        9.67    ******************                                             O
    105.8396          3.       1.00      91.33        8.67    ********                                                        O
    108.1837          3.       1.00      92.33        7.67    ********                                                         O
    110.5277          8.       2.67      95.00        5.00    ********************                                               O
    112.8718          2.       0.67      95.67        4.33    ******                                                             O
    115.2159          3.       1.00      96.67        3.33    ********                                                            O
    117.5600          2.       0.67      97.33        2.67    ******                                                              O
    119.9041          5.       1.67      99.00        1.00    *************                                                        O
    122.2482          2.       0.67      99.67        0.33    ******                                                                O
    124.5923          1.       0.33     100.00        0.00    ***                                                                   O
```

TABLE 3. NET AVERAGE ECONOMIC COST-PCB WASTES

```
NUMBER OF ITERATIONS =   300          MEAN =          31.70612               STANDARD DEVIATION =         7.56760
                                   MINIMUM =          11.17426         COEFFICIENT OF VARIATION, % =       23.86796
                                   MAXIMUM =          52.33400

    LOWER NUMBER OF   PERCENT  CUMULATIVE  CUMULATIVE                           DISTRIBUTIONS
    LIMIT   ENTRIES   ENTRIES   % ENTRIES  COMPLEMENT   * = FREQUENCY DISTRIBUTION     O = CUMULATIVE FREQUENCY DISTRIBUTION

  10.1514        1.      0.33        0.33       99.67   O**
  11.5834        1.      0.33        0.67       99.33   O**
  13.0154        0.      0.00        0.67       99.33   O
  14.4475        1.      0.33        1.00       99.00   *O*
  15.8735        2.      0.67        1.67       98.33   *O***
  17.3115        9.      3.00        4.67       95.33   ***O*****************
  18.7435        4.      1.33        6.00       94.00   ****O*****
  20.1756        1.      0.33        6.33       93.67   *** O
  21.6076       12.      4.00       10.33       89.67   *******O*******************
  23.0396       11.      3.67       14.00       86.00   **********O**************
  24.4716       15.      5.00       19.00       81.00   *************O********************
  25.9036       28.      9.33       28.33       71.67   ********************O*****************************************
  27.3357       28.      9.33       37.67       62.33   **************************O***********************************
  28.7677       21.      7.00       44.67       55.33   *******************************O***************
  30.1987       32.     10.67       55.33       44.67   ***************************************O*******************************
  31.6317       25.      8.33       63.67       36.33   *********************************************O**********
  33.0638       14.      4.67       68.33       31.67   ********************************                O
  34.4958       16.      5.33       73.67       26.33   ************************************                O
  35.9278       17.      5.67       79.33       20.67   **************************************                  O
  37.3598       13.      4.33       83.67       16.33   *****************************                              O
  38.7918        7.      2.33       86.00       14.00   ****************                                            O
  40.2239        9.      3.00       89.00       11.00   *********************                                         O
  41.6559        5.      1.67       90.67        9.33   ************                                                   O
  43.0879        8.      2.67       93.33        6.67   *******************                                              O
  44.5199        5.      1.67       95.00        5.00   ************                                                       O
  45.9520        3.      1.00       96.00        4.00   ********                                                           O
  47.3840        5.      1.67       97.67        2.33   ************                                                        O
  48.8160        4.      1.33       99.00        1.00   **********                                                           O
  50.2480        1.      0.33       99.33        0.67   ***                                                                   O
  51.6801        2.      0.67      100.00        0.00   *****                                                                 O
```

TABLE 4. NET ANNUAL AVERAGE OPERATING COSTS-PCB WASTES

PERIOD	COUNT	MEAN	STANDARD DEVIATION	COEF. OF VARIATION	MINIMUM	MAXIMUM	COEF. OF SKEWNESS	COEF. OF KURTOSIS
1	300.	30.68743	9.42636	30.71	8.71840	60.33244	0.21 (1.50)	-0.02 (0.09)
2	300.	27.97160	10.45899	37.39	0.48786	56.68623	0.14 (1.01)	-0.38 (1.35)
3	300.	23.60573	12.69471	53.78	-6.24827	60.32095	0.32 (2.26)	-0.03 (0.12)
4	300.	19.16311	13.60041	70.97	-14.91788	58.46643	0.19 (1.38)	-0.03 (0.11)
5	300.	13.07835	14.85218	113.56	-20.04438	58.92078	0.24 (1.71)	-0.08 (0.23)
6	300.	4.89344	16.82818	343.89	-38.94235	56.92928	-0.03 (0.20)	-0.02 (0.09)
7	300.	-1.96219	20.80541	1060.32	-68.87634	51.86911	-0.15 (1.08)	0.14 (0.50)
8	300.	-11.75791	25.35637	215.65	-69.69920	57.14721	-0.02 (0.18)	-0.45 (1.59)
9	300.	-23.33296	30.78233	131.93	-107.74347	57.68674	-0.14 (0.99)	-0.04 (0.13)
10	300.	-36.26134	34.17023	94.23	-140.81348	51.55303	-0.15 (1.10)	0.06 (0.21)
11	300.	-50.92933	42.37305	83.20	-189.53712	55.35488	-0.19 (1.38)	-0.18 (0.63)
12	300.	-71.72401	47.15552	65.75	-219.04622	37.89673	-0.31 (2.20)	0.10 (0.35)
13	300.	-96.26329	56.52714	58.72	-262.56143	105.12555	-0.14 (1.01)	0.62 (2.22)
14	273.	-114.14446	67.06186	58.75	-282.49850	56.11337	-0.15 (1.04)	-0.09 (0.30)
15	236.	-142.76257	76.90813	53.87	-342.07401	57.73023	0.00 (0.02)	-0.10 (0.32)
16	78.	-181.00525	87.45088	48.31	-452.43469	-2.92723	-0.38 (1.40)	0.30 (0.56)
17	33.	-190.56729	118.02286	61.93	-549.70239	-3.45014	-0.76 (1.85)	1.07 (1.33)

($8.00) and overhead at (220%).

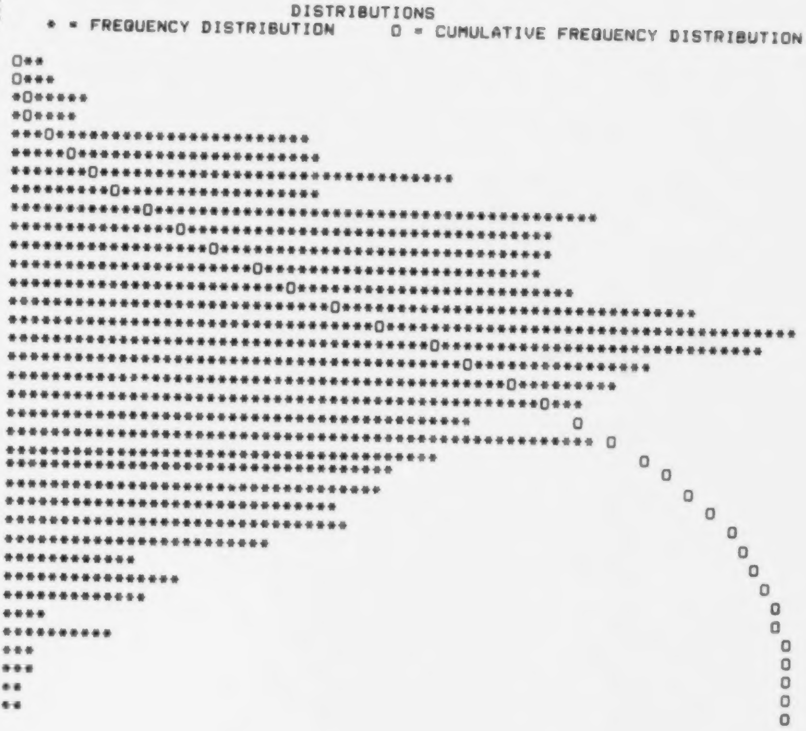
The results of these assumptions are shown in Table 5. The mean estimate is $1700, with a cummulative probability of about 55%. We suggest that these figures represent the incremental cost of adding uncertainty analysis to an engineering cost study.

TABLE 5. COST OF UNCERTAINTY ANALYSIS

```
NUMBER OF ITERATIONS =  1000          MEAN =      1718.30640                STANDARD DEVIATION =       274.63239
                                   MINIMUM =      1092.67004         COEFFICIENT OF VARIATION, % =      15.98274
                                   MAXIMUM =      2533.58716

      LOWER   NUMBER OF    PERCENT  CUMULATIVE  CUMULATIVE
      LIMIT     ENTRIES    ENTRIES   % ENTRIES  COMPLEMENT

  1066.6194          2.       0.20        0.20       99.80
  1107.8881          3.       0.30        0.50       99.50
  1149.1567          6.       0.60        1.10       98.90
  1190.4254          5.       0.50        1.60       98.40
  1231.6941         24.       2.40        4.00       96.00
  1272.9628         25.       2.50        6.50       93.50
  1314.2314         36.       3.60       10.10       89.90
  1355.5001         25.       2.50       12.60       87.40
  1396.7688         48.       4.80       17.40       82.60
  1438.0375         45.       4.50       21.90       78.10
  1479.3062         45.       4.50       26.40       73.60
  1520.5748         44.       4.40       30.80       69.20
  1561.8435         46.       4.60       35.40       64.60
  1603.1122         57.       5.70       41.10       58.90
  1644.3809         65.       6.50       47.60       52.40
  1685.6495         62.       6.20       53.80       46.20
  1726.9182         53.       5.30       59.10       40.90
  1768.1869         50.       5.00       64.10       35.90
  1809.4556         47.       4.70       68.80       31.20
  1850.7242         38.       3.80       72.60       27.40
  1891.9929         48.       4.80       77.40       22.60
  1933.2616         35.       3.50       80.90       19.10
  1974.5303         32.       3.20       84.10       15.90
  2015.7990         31.       3.10       87.20       12.80
  2057.0676         27.       2.70       89.90       10.10
  2098.3364         28.       2.80       92.70        7.30
  2139.6052         21.       2.10       94.80        5.20
  2180.8740         10.       1.00       95.80        4.20
  2222.1428         14.       1.40       97.20        2.80
  2263.4116         11.       1.10       98.30        1.70
  2304.6804          3.       0.30       98.60        1.40
  2345.9492          8.       0.80       99.40        0.60
  2387.2180          2.       0.20       99.60        0.40
  2428.4868          2.       0.20       99.80        0.20
  2469.7556          1.       0.10       99.90        0.10
   OVERFLOW          1.       0.10      100.00        0.00
```



AN ASSESSMENT OF EMISSIONS FROM A HAZARDOUS WASTE INCINERATION FACILITY

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ABSTRACT

The exposure in a nearby population to volatile organic compounds (VOCs) from emissions of a municipal hazardous waste incinerator is determined by measuring the emission rates and estimating the dispersion of those pollutants over the surrounding community. Measurements of fugitive VOC emissions from leaky pipe fittings, flanges, pumps, and valves are made. VOC emissions from the stack and air pollution control devices are also measured. An emission assessment is then performed to determine the percentage concentration and population exposure associated with selected emissions from each source at the facility. Results indicate that, in this particular case, fugitive and stack emissions do not contribute significantly to pollutant concentration and population exposure. Further, data for specific constitutents of the VOC emissions also show extremely low concentrations and exposure, but these results are based on only a partial analysis and additional qualitative emission analyses are required.

INTRODUCTION

Incineration of hazardous wastes produces stack and nonstack emissions. Until now, the Environmental Protection Agency (EPA) has been concentrating on minimizing stack emissions. EPA has begun to suspect, however, that stack emissions may not be the predominant source of air emissions from hazardous waste incinerators. To better characterize all sources of air pollution from these facilities, EPA has entered into a three-year interagency agreement with the Department of Energy at Oak Ridge National Laboratory (DOE/ORNL) to determine the relative magnitude and significance of stack and nonstack emissions, and to ultimately evaluate potential control techniques.

Although stack testing is not new and fugitive emissions measurements have been made at oil refineries and chemical plants, stack and fugitive emissions measurements have not been made simultaneously at the same hazardous waste facility. Since this is essential for comparison, EPA decided to do it at the first available opportunity.

This paper presents results of an experiment conducted at the liquid fluid incinerator operated by Cincinnati's Metropolitan Sewer District (MSD) in July 1981. The purpose of the experiment was to determine for one set of conditions the population exposure to hydrocarbons that are emitted by an incinerator. Hydrocarbon emission rates from both stack and nonstack sources were measured. Atmospheric concentrations were estimated from these measurements using the Industrial Source Complex Dispersion (ISC) model (3). Population exposure to these concentrations were then calculated. Using toxicity data for six principal organic hazardous constituents (POHCs) contained in the hydrocarbon emissions, the significance of these exposures was assessed.

This experiment represents the first attempt EPA has made to measure both stack and nonstack emissions simultaneously at one incinerator. Consequently, it is premature to draw broad general conclusions about the relative significance of stack and fugitive emissions at hazardous waste incinerators from the work completed thus far.

Source Term Development

The Cincinnati MSD incinerator is a two-year old facility with a thermal capacity of 3.50 x 10^{10} cal/hr (139 x 10^6 Btu/hr). It consists of a rotary kiln and a liquid injection furnace in parallel followed by a secondary combustion chamber, quench, high pressure venturi scrubber, and packed bed absorber. Nitrogen blanked tanks, 9.46 x 10^4 l (25,000 gallons), allow for storage of liquid waste which is typically delivered by tank truck.

Prior to conducting field measurements, fugitive emission rates were estimated using emission factors for valves, flanges, and pumps developed from studies of oil refineries (8). These calculations indicated that, indeed, fugitive emissions may greatly exceed stack emissions at 99.99 percent DRE and may be significant at lower destruction and removal efficiencies.

Results of these calculations are shown in Figure 1 (7). To gather some preliminary information to determine the validity of these calculations, EPA monitored the fugitive emissions at the Cincinnati incinerator during a trial burn at which stack testing was conducted.

During the trial burn, approximately 3.41 x 10^5 l (90, 000 gallons) of waste containing chlorinated compounds as well as alcohols, carbonyl compounds, and C_6 - C_8 alkanes from nearby landfills were burned. Hydrocarbon stack emissions, measured as methane, were determined using the Dohrmann DC-50 continuous monitor as a direct flame ionization detector (1). Fugitive hydrocarbon emissions were determined by screening each valve, vent, flange, and pump seal in the storage, loading dock, and at the feed inlets to the incinerators using the Century Systems OVA 108 and OVA 128 portable organic vapor analyzers and EPA standard Reference Method 21 (6). Both instruments were calibrated to methane and indicated hydrocarbon concentrations in ppm methane. These readings were converted to emission rates in g/hr using correlations developed in another study (5).

Modeling Methodology

The impact of these emissions on the surrounding population was assessed using the Industrial Source Complex Dispersion Model. Together with local meteorological and population data supplied by ORNL, the model can be used to assess the air quality impact of emissions from area and point sources associated with an industrial complex. The model assumes Gaussian plume dispersion and can account for the effects of elevated terrain surrounding the incinerator and building wake effects. Using meteorological data and incinerator design, operation, and emission release data (Table 1), the ISC computer model was run to estimate downwind concentrations at 176 receptors (16 directions and 11 distances) (see Figure 2). Each receptor point was defined by the intersection of 1 of 11 rings of various diameters centered around the incinerator and 1 of 16 radial lines emanating from the complex center. Each radial was separated by 22.5° intervals beginning with due north (0°) and proceeding clockwise. The 11 ring diameters were 0.2, 0.3, 0.5, 0.7, 1.0, 2.0, 3.0, 5.0, 7.0, 10.0, and 15.0 km. These distances were chosen to span the greater Cincinnati metropolitan area.

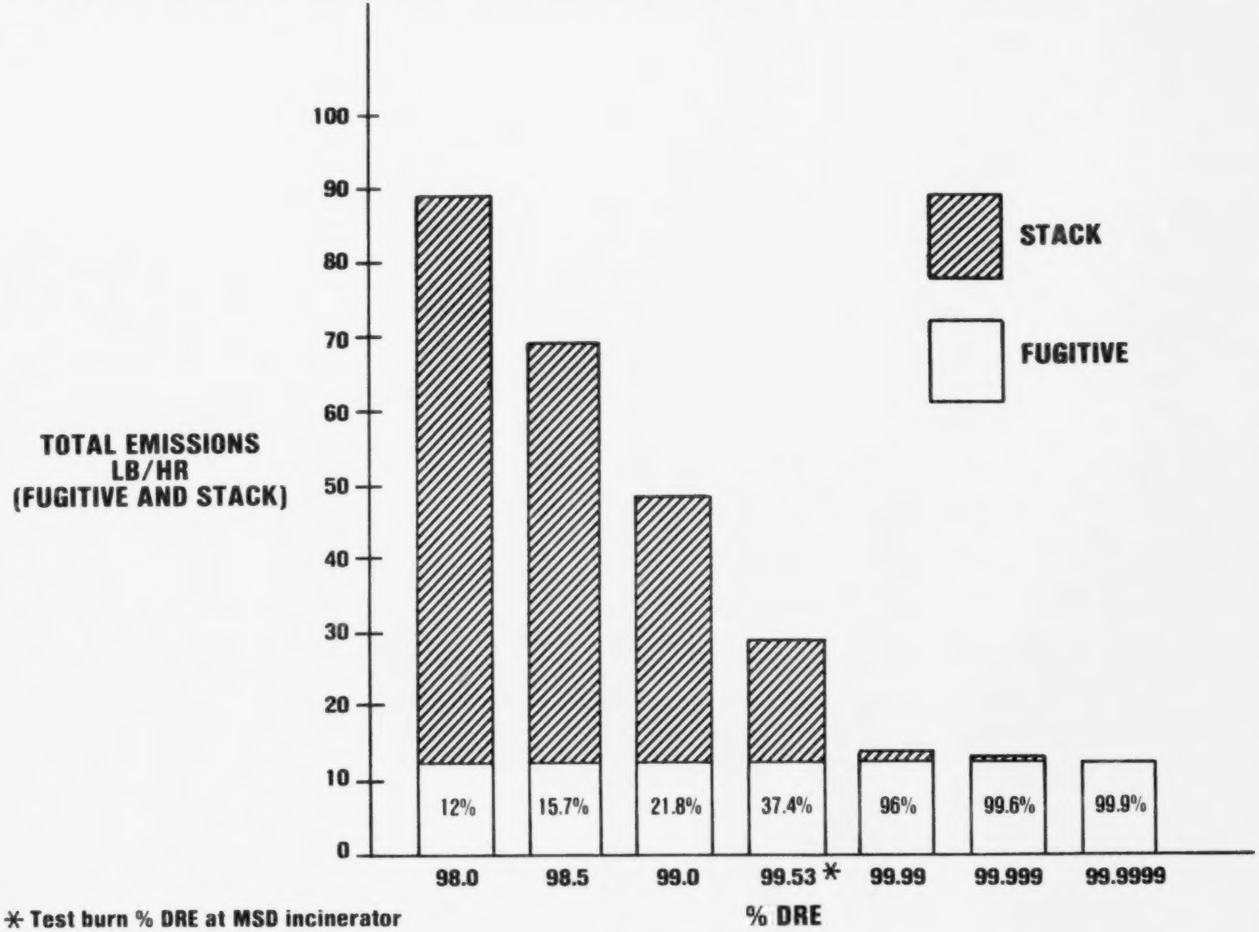
To account for Cincinnati's hilly terrain, elevations of each receptor point were taken from topographic maps. At 91 of the 176 receptor locations where the elevation exceeded the stack height, the stack height elevation less 30.5 cm (1 ft) was used. Such treatment may be simplified, but it's conservative in that the concentration calculated at this elevation would be the maximum experienced at that particular location.

The concentration calculated by ISC were than coupled with 1980 census data to give population exposures (2, 4).

RESULTS

Downwind concentration estimates at the 176 receptors were calculated for total

PERCENTAGE FUGITIVE EMISSIONS AS A FUNCTION OF % DRE



* Test burn % DRE at MSD incinerator

FIGURE 1

Table 1. Summary of source values used to represent the Cincinnati MSD incinerator

Source name	Representation	Component number	Size (m^2)	Coordinates of center (m)	Release height (m)	Release velocity (m/s)	Gas temperature (K)	Pollutant emission rates, $g/s^{b,c}$						
								Total HC[d]	$CHCl_3$[e]	CCl_4[f]	C_2Cl_4[g]	HCCP[h]	C_2Cl_6[i]	C_6Cl_6[j]
Stack	1 stack	1	3.4[a]	35.0, 0:0	27.4	6.40	366.5	5.64×10^{-1}	5.17×10^{-4}	7.01×10^{-5}	3.05×10^{-4}	6.52×10^{-6}	1.77×10^{-5}	1.64×10^{-5}
Structure	2 area sources	1	62.8	26.5, 4.0	20.1			1.43×10^{-3}	1.99×10^{-6}	8.10×10^{-7}	4.30×10^{-8}	2.60×10^{-9}	5.77×10^{-10}	1.14×10^{-10}
		2	62.8	18.5, 4.0	20.1			1.43×10^{-3}	1.99×10^{-6}	8.10×10^{-7}	4.30×10^{-8}	2.60×10^{-9}	5.77×10^{-10}	1.14×10^{-10}
Tank farm	3 area sources	1	455.2	-33.6, 9.5	6.1			1.04×10^{-2}	1.44×10^{-5}	5.87×10^{-6}	3.11×10^{-7}	1.88×10^{-8}	4.18×10^{-9}	8.29×10^{-10}
		2	455.2	-54.9, 9.5	6.1			1.04×10^{-2}	1.44×10^{-5}	5.87×10^{-6}	3.11×10^{-7}	1.88×10^{-8}	4.18×10^{-9}	8.29×10^{-10}
		3	455.2	-76.3, 9.5	6.1			1.04×10^{-2}	1.44×10^{-5}	5.87×10^{-6}	3.11×10^{-7}	1.88×10^{-8}	4.18×10^{-9}	8.29×10^{-10}
TOTAL								5.98×10^{-1}	5.64×10^{-4}	8.93×10^{-5}	3.06×10^{-4}	6.58×10^{-6}	1.77×10^{-5}	1.64×10^{-5}

[a] Stack area corresponds to an inner diameter of 2.08 m.

[b] Stack emission rates calculated from stack sampling.

[c] Fugitive emission rates calculated from waste chemical analyses.

[d] Total hydrocarbon.

[e] Chloroform – specified primary organic hazardous constituent (POHC).

[f] Carbon tetrachloride – specified POHC.

[g] Tetrachlorethene – specified POHC.

[h] Hexachlorocyclopentadiene – specified POHC.

[i] Hexachlorethane – specified POHC.

[j] Hexachlorobenzene – specified POHC.

RECEPTOR GRID

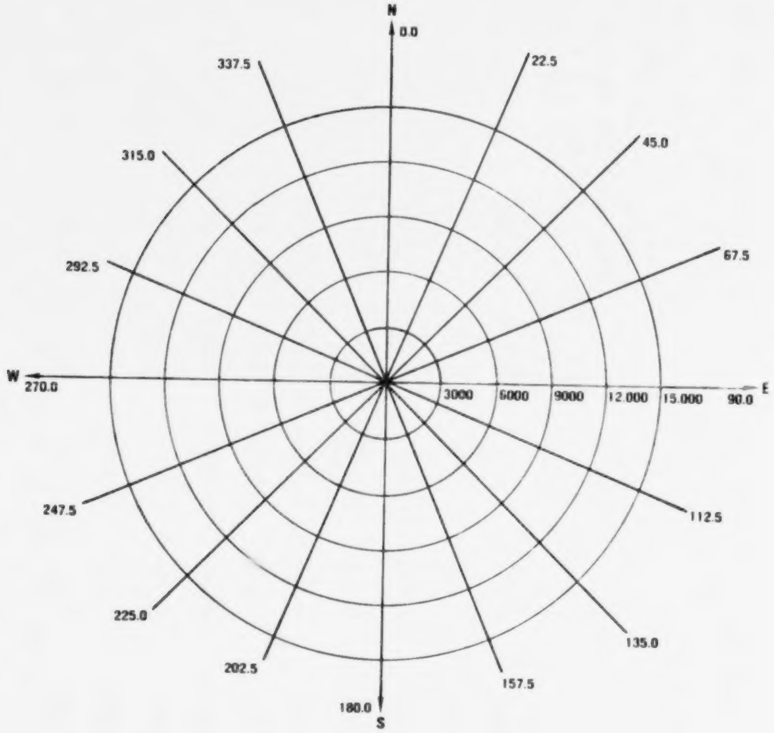


FIGURE 2

Table 2. Fractional contribution of each source to total ground level air concentration of HC

Distance (m)	Stack		Structure		Tank farm	
	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum
200	0.348	0.929	0.003	0.050	0.039	0.648
300	0.409	0.946	0.004	0.037	0.034	0.587
500	0.521	0.932	0.007	0.023	0.052	0.471
700	0.596	0.919	0.009	0.018	0.068	0.393
1,000	0.674	0.901	0.010	0.015	0.086	0.314
2,000	0.774	0.915	0.008	0.011	0.076	0.215
3,000	0.816	0.917	0.007	0.010	0.076	0.174
5,000	0.867	0.920	0.006	0.008	0.073	0.125
7,000	0.874	0.922	0.006	0.008	0.072	0.118
10,000	0.918	0.923	0.006	0.006	0.071	0.076
15,000	0.921	0.925	0.005	0.006	0.070	0.073

TABLE 3

LOCATIONS AND VALUES OF MAXIMUM AVERAGE GROUND LEVEL AIR CONCENTRATIONS

POLLUTANT	SOURCE	CONCENTRATION, MICROGRAMS PER CUBIC METER	LOCATION OF CENTROID	
			DEGREES FROM NORTH	METERS FROM ORIGIN
CHCL3	STACK	1.33E-03	348.75	250.00
CHCL3	STRUCTURE	5.59E-05	326.25	250.00
CHCL3	TANK FARM	7.32E-04	11.25	250.00
CHCL3	ALL SOURCES	1.86E-03	348.75	250.00
CCL4	STACK	1.80E-04	348.75	250.00
CCL4	STRUCTURE	2.27E-05	326.25	250.00
CCL4	TANK FARM	2.98E-04	11.25	250.00
CCL4	ALL SOURCES	4.52E-04	11.25	250.00
C2CL4	STACK	7.82E-04	348.75	250.00
C2CL4	STRUCTURE	1.21E-06	326.25	250.00
C2CL4	TANK FARM	1.58E-05	11.25	250.00
C2CL4	ALL SOURCES	7.93E-04	348.75	250.00
HCCP	STACK	1.67E-05	348.75	250.00
HCCP	STRUCTURE	7.31E-08	326.25	250.00
HCCP	TANK FARM	9.53E-07	11.25	250.00
HCCP	ALL SOURCES	1.75E-05	348.75	250.00
C2CL6	STACK	4.54E-05	348.75	250.00
C2CL6	STRUCTURE	1.62E-08	326.25	250.00
C2CL6	TANK FARM	2.12E-07	11.25	250.00
C2CL6	ALL SOURCES	4.56E-05	348.75	250.00
C6CL6	STACK	4.20E-05	348.75	250.00
C6CL6	STRUCTURE	3.21E-09	326.25	250.00
C6CL6	TANK FARM	4.19E-08	11.25	250.00
C6CL6	ALL SOURCES	4.21E-05	348.75	250.00

TABLE 4

SUMMARY OF EXPOSURES TO 877641. PERSONS AT
CINCINNATI MSD INCINERATOR - POHC RUN

POLLUTANT	SOURCE	TOTAL EXPOSURE, PERSON*UG/M**3	AVERAGE INDIVIDUAL EXPOSURE, UG/M**3
CHCL3	STACK	3.30E+01	3.75E-05
CHCL3	STRUCTURE	4.33E-01	4.94E-07
CHCL3	TANK FARM	5.22E+00	5.95E-06
CHCL3	ALL SOURCES	3.87E+01	4.41E-05
CCL4	STACK	4.47E+00	5.09E-06
CCL4	STRUCTURE	1.76E-01	2.01E-07
CCL4	TANK FARM	2.13E+00	2.42E-06
CCL4	ALL SOURCES	6.80E+00	7.74E-06
C2CL4	STACK	1.94E+01	2.22E-05
C2CL4	STRUCTURE	9.35E-03	1.07E-08
C2CL4	TANK FARM	1.13E-01	1.28E-07
C2CL4	ALL SOURCES	1.96E+01	2.23E-05
HCCP	STACK	4.16E-01	4.74E-07
HCCP	STRUCTURE	5.66E-04	6.45E-10
HCCP	TANK FARM	6.82E-03	7.78E-09
HCCP	ALL SOURCES	4.23E-01	4.82E-07
C2CL6	STACK	1.13E+00	1.29E-06
C2CL6	STRUCTURE	1.26E-04	1.43E-10
C2CL6	TANK FARM	1.51E-03	1.73E-09
C2CL6	ALL SOURCES	1.13E+00	1.29E-06
C6CL6	STACK	1.05E+00	1.19E-06
C6CL6	STRUCTURE	2.49E-05	2.83E-11
C6CL6	TANK FARM	3.00E-04	3.42E-10
C6CL6	ALL SOURCES	1.05E+00	1.19E-06
ALL HC	STACK	3.60E+04	4.10E-02
ALL HC	STRUCTURE	3.12E+02	3.55E-04
ALL HC	TANK FARM	3.76E+03	4.28E-03
ALL HC	ALL SOURCES	4.01E+04	4.57E-02

hydrocarbon (HC) releases and for release values of six specified principal organic hazardous constituents (POHCs). Concentrations at the 176 receptors were calculated for each of three sources and total for the seven pollutants (HC + 6 POHCs). The three sources were stack emissions, fugitive emissions from the incinerator structure, and fugitive emissions from the tank farm area.

Total Hydrocarbon Air Concentration

For all directions, the maximum concentration occurred immediately downwind. Not surprisingly, the average concentrations decrease rapidly with distance to less than 2 percent of the maximum at a distance of 12.5 km downwind.

Contribution of Sources to HC Concentration

As one might expect, the relative contribution to total ground level HC by each of the three release types varies with both distance and direction from the facility. Table 2 summarizes the relative contribution of each of the three sources to total ground level air concentration of HC as a function of distance.

POHC Air Concentration

With fugitive and stack data available for six POHCs, a more detailed emission/exposure assessment is possible Table 3 contains maximum concentration and location data for six identified POHCs. The largest POHC concentration is $1.86 \times 10^{-3} \mu g/m^3$ (3.75×10^{-7} ppm) of chloroform ($CHCl_3$) occurring in the sector segment described by the centroid location of 250 m from the incinerator on an angle of 348.75° clockwise from due north. This concentration is very low, as is the concentration of the most toxic POHC, hexachlorocyclopentadiene (HCCP), has a maximum concentration of $1.75 \times 10^{-5} \mu g/m^3$ (1.54×10^{-9} ppm).

Population Exposure to POHC

Exposures to POHCs are also very low. Total exposure (person-$\mu g/m^3$) ranges from 1.05 for C_6Cl_6 to 38.7 for $CHCl_3$ while average individual exposure (person-$\mu g/m^3$) ranges from 1.19×10^{-6} for C_6Cl_6 to 4.41×10^{-5} for $CHCl_3$. Table 4 also contains the total exposure and average individual exposure to each POHC from each source. Clearly, most POHC exposure is due to stack releases, but significant exposure can also be due to fugitive releases when the POHC is volatile ($CHCL_3$ and CCl_4 have the highest vapor pressure of the identified POHCs so their fugitive emission rates are higher). For example, over 14 percent of total exposure to CHC[illegible] is caused by fugitive releases whereas only about 0.03 percent of total exposure to semi-volatile C_6Cl_6 is caused by fugitive releases.

CONCLUSIONS

Public exposure to HC from this incinerator is low. An assessment of emission sources shows that from the site 89.8 percent of total exposure to HC is due to stack emissions, but that for locations close to the incinerator, fugitive HC sources may dominate (5). Perhaps, because they are emitted near the ground, fugitive emissions have a disproportionately high effect on close-in population exposure.

The methodology employed to measure fugitive emissions has limitations in accuracy and composition identification. For example, actual samples could have been taken of the gas emitted from fugitive leaks to verify the chemical composition of the leak and the leak rate, but shortages of both time and money prevented this. Nevertheless, results of this study are useful. Not only are future research areas defined, but also this study is based on measured data which, with future measurement, can be used to characterize emissions from hazardous waste incinerators.

The emission assessment used data from a test burn for a very well run incinerator which achieved destruction efficiencies that met or exceeded the 99.99 percent DRE standard. (In addition, the facility was new and, therefore, would not be expected to have as many fugitive emissions as an older less well maintained facility.) This data reflects only one day of operation which is extrapolated to annual operation, a simplifying assumption that may lead to large source term inaccuracies. The validity of this assumption needs to be studied. The possibility of large, short-term releases due to accidents, spills, and sprays should also be investigated. If it is assumed that day to day operation is similar to test burn conditions, then it seems reasonable to conclude that normal incinerator operation at or exceeding the standard levels produces minimum HC emissions. Conclusions concerning total hydrocarbon exposure require additional qualitative and quantitative composition analyses.

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CHARACTERIZATION OF HAZARDOUS WASTES

GENERATED BY THE PESTICIDE MANUFACTURING INDUSTRY

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ABSTRACT

The paper describes a program conducted to characterize waste streams from pesticide manufacturing processes to determine whether they should be considered as toxic hazardous wastes under Section 3001 of the Resource Conservation and Recovery Act (RCRA). The program is being conducted by EPA's Office of Research and Development, Industrial Environmental Research Laboratory, Research Triangle Park, NC, in support of the Agency's Office of Solid Waste. The study was initiated by classifying pesticide products and ranking them by such factors as production volume, toxicity, bioaccumulation, and persistence. The rankings were then used to select those production processes to be analyzed. For each process selected, an Engineering Analysis is conducted to define the process chemistry and determine potential hazardous waste streams. These waste streams are then sampled at an operating pesticide manufacturing plant. The samples are analyzed for those parameters necessary to make a hazardous waste determination, such as: chemical composition, corrosivity (pH), reactivity, and EP toxicity. The analytical results will be combined with the engineering analysis and presented to the Office of Solid Waste in appropriate background reports.

INTRODUCTION

Purpose

EPA's Office of Research and Development, Industrial Environmental Research Laboratory, Research Triangle Park, NC, is conducting a study for the Agency's Office of Solid Waste (OSW) to characterize waste streams from pesticide manufacturing plants. The purpose of the characterization is to enable OSW to determine whether specific waste streams should be listed as toxic hazardous wastes under Section 3001 of the Resource Conservation and Recovery Act (RCRA).

The study is being supported by five contracts: a contract with TRW to perform engineering analyses and assist ORD in overall project coordination and liaison; three contracts (with TRW, A. D. Little, and Battelle Columbus Laboratories) to conduct on-site sampling and laboratory analyses of pesticide manufacturing waste streams; and contract with the Research Triangle Institute to perform QA/QC audits of the sampling and analysis phases of the study.

Scope

Ideally, the study would evaluate all waste streams within the pesticide industry; however, the magnitude of the industry (92 corporate producers, 141 production facilities, 288 pesticide products)* precluded 100% coverage within the project's budget and time frame. Thus, priorities were established to provide broad coverage of the pesticide manufacturing industry. It is emphasized that this selection procedure does not presume that the waste streams from the processes selected for evaluation are, in fact, hazardous, nor is it presumed that other processes do not produce hazardous wastes Only a careful technical evaluation can determine whether a specific waste stream is hazardous.

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* Based on 1978 data

INDUSTRY CHARACTERIZATION

As discussed above, it was necessary to develop priorities for directing evaluations of processes within the pesticide manufacturing industry. This was accomplished in three steps:

1) Classification of Pesticides
2) Ranking of Pesticides
3) Selection of Processes to be Evaluated

Pesticide Classification

Pesticides can be classified in various ways, including by:

a) Use, and
b) Chemical Structure

a) Pesticide Use

Classifying pesticides by use results in the following breakdown:

- Insecticide (I)
- Herbicide (H)
- Fungicide (F)
- Nematicide & Fumigant (N)
- Rodenticide (R)
- Plant Growth Regulator (P)

b) Chemical Structure

Pesticides can be classified by chemical structure into the following categories:

I. Chlorinated Hydrocarbons
II. Organophosphates
III. Carbamates
IV. Triazines
V. Anilides
VI . Organometallics
VII. General Nitrogenous
VIII. Diene-based
IX. Ureas & Uracils
X. Nitrated Hydrocarbons
XI. Miscellaneous

Since the wastes produced in any process are a function of process chemistry, the classification by chemical structure was deemed more appropriate than pesticide use.

Pesticide Ranking

The pesticide processes were ranked according to the following parameters [Kelso, et al. (2)]:

- Production Volume
- Acute Toxicity of the Pesticide
- Special Toxicity of the Pesticide
- Acute Toxicity of the Raw Material
- Special Toxicity of the Raw Material
- Persistence of the Pesticide
- Bioaccumulation of the Pesticide

For each of the 288 pesticides identified, each parameter was scored zero through four, with zero indicating no impact and four indicating maximum impact. The parameter values were then summed to give a total value for each pesticide [Harden, et al. (1)].

Selection of Processes

Three criteria were used to select the pesticide processes to be evaluated:

1) Chemical Classification

For each of the 11 chemical classifications, it was desirable to have several processes represented.

2) Pesticide Rank

Higher ranked pesticides were given priority over those with lower scores.

3) Current Production

Many pesticides on the initial list are no longer produced. Only those in current production or planned for future manufacture were considered for evaluation.

Using the above three criteria, 22 pesticide manufacturing plants covering 73 pesticide processes were initially selected for evaluation.

STUDY DESIGN

Each pesticide manufacturing process selected for evaluation is subjected to a rigorous analysis involving several elements:

Engineering Analysis

Using information available in the literature as well as other information available through EPA, an engineering analysis is conducted for each process. This analysis produces the following information:

1) Pesticide Properties (e.g., use and chemical classification, chemical name and structure, molecular weight, physical properties, solubility, and toxicity).
2) Raw Materials.
3) Process Description and Flow Diagram.
4) Process Chemistry (including discussions of chemical reactions and side-reactions).
5) Waste Stream Descriptions (including potential chemical composition).
6) Waste Disposal Methods (based on current on-site practices).
7) Sampling Recommendations (i.e, designation of waste streams to be sampled at an operating facility).

Pre-Sampling Site Visit

A pre-sampling site visit is made to each facility to be sampled. The purposes of the visit are:

1) Determine the accuracy and completeness of the engineering analysis. (The analysis is sent to the facility for review prior to the visit.)
2) Determine accessibility to sampling locations via an in-plant evaluation.
3) Answer questions raised by industry personnel.
4) Determine sampling dates convenient to the plant and consistent with production schedules.

Sampling and Analysis Plan

Subsequent to the pre-sampling site visit, necessary corrections are made to the engineering analysis, and a sampling and analysis plan is prepared covering the following for each process:

- Process Flow Diagram (revised as necessary)
- Identification of Sampling Locations
- Specification of:
  - Sample Code Numbers
  - Sampling Devices and Containers
  - Sample Volumes and Repetitions
  - Chain of Custody Procedures
  - Safety Requirements
- Specification of Analytical Procedures
  - Defined for Each Sample
  - Referenced to Protocol Manual[+]

This plan, prepared by the Sampling and Analysis Contractor, is reviewed by OSW and ORD. When approved, it is sent to the pesticide plant prior to the actual sampling.

On-Site Sampling

Sampling is conducted at the facility in accordance with the Sampling and Analysis Plan. The samples are handled and shipped in accordance with regulations regarding transportation of hazardous materials.

[+] "Sampling and Analysis Procedures for Pesticide Manufacturing Wastes," prepared for EPA by A. D. Little, Inc., under Contract No. 68-02-3111, Task Directive No. 123.

Laboratory Analysis

The samples are sent to the contractor's laboratory and analyzed according to the Sampling and Analysis Plan. The Protocol Manual defines the analytical procedures; however, modifications to the procedures may be required depending on the nature of the wastes. Parameters to be determined include chemical composition, corrosivity, reactivity, and EP toxicity. The range of analytical procedures includes pH, TOC, SSMS, ICAP/AA, HPLC, GS/FID, GS/MS, FTIR. The procedures selected for each sample depend upon the expected composition.

QA/QC

The study is being conducted under a Quality Assurance/Quality Control Program developed and directed by the Technical Support Staff (TSS) of EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC. Each of the three sampling and analysis contractors is subject to QA/QC audits by the Research Triangle Institute, TSS's QA/QC contractor, including:

- Sampling Audits
- Laboratory Performance Audits
- Data Validation Audits

In addition, each sampling and analysis contractor has prepared and revised a QA/QC plan which has been approved by TSS.

PROGRAM OUTPUTS

The study will result in the delivery to OSW of a background report for each pesticide process evaluated. These reports will include engineering analyses, the results of the sampling and analysis effort, and, if available, supplementary information gathered in response to RCRA Section 3007 questionnaires sent to the pesticide producers by OSW. The reports will be used by OSW as input to the process of determining whether or not a specific waste stream should be listed as a toxic hazardous waste under Section 3001 of RCRA. The reports will also be used as supporting information for the waste management studies being conducted by OSW.

PROGRAM STATUS

The study was initiated in April 1981. Process/plant selection was completed in June, at which time contacts were made with the selected plants and confidentiality agreements negotiated between the contractors and the manufacturers. The initial pre-sampling meeting was conducted in September, and the first samples were collected in October. As of December, preliminary engineering analyses had been completed for 6 plants/22 processes; presampling visits made to 4 plants/16 processes; and sampling and analysis completed at 2 plants/4 processes.

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OVERVIEW OF INDUSTRY STUDIES PROGRAM

by

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INTRODUCTION

The Environmental Protection Agency is conducting studies of selected industries to establish an extensive information base with regard to the generation and management of hazardous waste. The goal of the Agency is more effective regulation of such wastes. In a sense, the Industry Studies will become the basis for the next major phase of regulations under the Resource Conservation and Recovery Act of 1976 (RCRA), as amended.

EPA promulgated phase I of the hazardous waste regulations on May 19, 1980. This initial phase defined and listed hazardous wastes and established requirements for generators, transporters, and treatment, storage, and disposal facilities. Despite the scope of these regulations, they still constitute only the first major step toward the comprehensive regulation of hazardous waste. EPA promulgated phase II of the regulations in January and February of 1981. The phase II regulations set technical standards for specific types of hazardous waste facilities. These technical standards provide the basis for the issuance of permits to these facilities.

EPA also announced a third phase of rulemaking. This will involve further expansion and refinement of the lists of hazardous wastes and the promulgation of facility standards tailored to the degree and type of hazard posed by specific wastes or industries. The hazardous wastes Industry Studies will form the major information base for these tailored regulations.

OBJECTIVES

The objectives of the Industry Studies program are to:

- fulfill the mandate of RCRA Section 3001 which requires that EPA identify and characterize hazardous waste streams that should be subject to RCRA controls:
- develop waste management guidance and/or regulations tailored to degree and type of hazard;
- foster recycling/recovery/treatment practices as alternatives to land disposal;
- provide the decisionmaking information necessary to accomplish an integrated approach toward regulation of industry under RCRA and other acts.

APPROACH

The effective development, refinement, and implementation of the regulatory program in the future requires the rapid establishment of an extensive information base on the generation, composition, management and ultimate fate of wastes produced by industry. To this end, the Industry Studies program consists of two related components; a waste characterization component and a waste management assessment component.

The data gathered under the waste characterization component will determine the waste streams of concern from specific product/production processes for listing under 40 CFR Part 261.32 of Section 3001 of RCRA. The waste management component will assist in the waste listing effort by characterizing existing practices. Additionally it will develop an informational framework from which decision makers can select strategies for tailoring of management standards. This framework will provide an integrated approach to the type and degree of hazard posed by particular waste/environment/technology situations by means of a cross cutting analysis of various alternatives. The analysis will provide the necessary elements to fulfill the requirements of Executive Order 12291 which calls for a Regulatory Impact Analysis (RIA) for proposed regulatory actions.

STATUS

Studies are currently underway in various industry segments of the organic chemical industry including:

- Industry Organic Chemicals
- Organic Chemical Products
    - Pesticides
    - Dyes
    - Pigments

THE INDUSTRY STUDIES PROGRAM: SYNTHETIC ORGANIC CHEMICALS INDUSTRY

by

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INTRODUCTION

The Resource Conservation and Recovery Act (RCRA) of 1976, under Section 3001, requires EPA to identify and list hazardous wastes. EPA's Office of Solid Waste (OSW) is currently pursuing studies to determine the waste streams from organic chemical production processes which should be listed as toxic under 40 CFR Part 261.32 of RCRA. EPA's Office of Research and Development (ORD) is providing assistance to OSW in this industry studies program. The industry segments assigned to ORD include pesticides, nonchlorinated industrial organic chemicals, and dyes and pigments. This paper summarize the approach and progress to date on the study of the synthetic organic chemicals industry (SOCMI) being conducted by EPA's Industrial Environmental Research Laboratory (IERL-Ci).

APPROACH

In the development of a program to assess the environmental impact of hazardous wastes from the chemical industry, it has been necessary to (1) break down the industry into manageable segments for study and (2) determine for each segment which product/processes are potential sources of hazardous wastes. Table 1 lists the industry breakdown into segments. It was agreed with OSW that IERL-Cincinnati would first address the industrial organics and the organic dyes and organic pigments segments of the industry; IERL-RTP would address pesticides. Other industry groups would be considered as funds become available.

In view of the magnitude of the industrial organics industry, (roughly 400 individual product/process configurations), it was important to establish an approach which would reduce the need for a plant sampling and analysis program to the absolute minimum since S&A is by far the most expensive phase of any such program. It was agreed that this approach would comprise the following steps:

1. Screening of the industrial organic product/processes to establish a basis for a priority ranking.

2. Selection of an initial 35 product/processes for detailed engineering analysis to determine: 1) if there are sufficient data for listing the wastes as hazardous; 2) if there are insufficient data but there is reason to pursue gathering additional data for listing purpose; and 3) there is sufficient reason for removing that product/process from further concern. This selection was done by IERL-Ci staff with OSW concurrence.

3. Those product/processes from the 35 which remain of concern would be subjected to site visits or supplemental questionnaires, and subsequent sampling and analysis where appropriate as per the logic diagram described in Figure 1.

Step 1 was carried out by IT Enviroscience using the data they had developed in their major study for OAQPS on the organic chemicals industry. The ITE report lists product/processes ranked on the basis of the total quantity of non-aqueous wastes. It was agreed with OSW that selection of the initial 35 product/processes for detailed engineering analysis would be based on that list. The following additional qualifications also were specified by OSW:

TABLE 1. SUMMARY OF DATA ON THE ORGANIC CHEMICALS PRODUCTS INDUSTRIES(1)

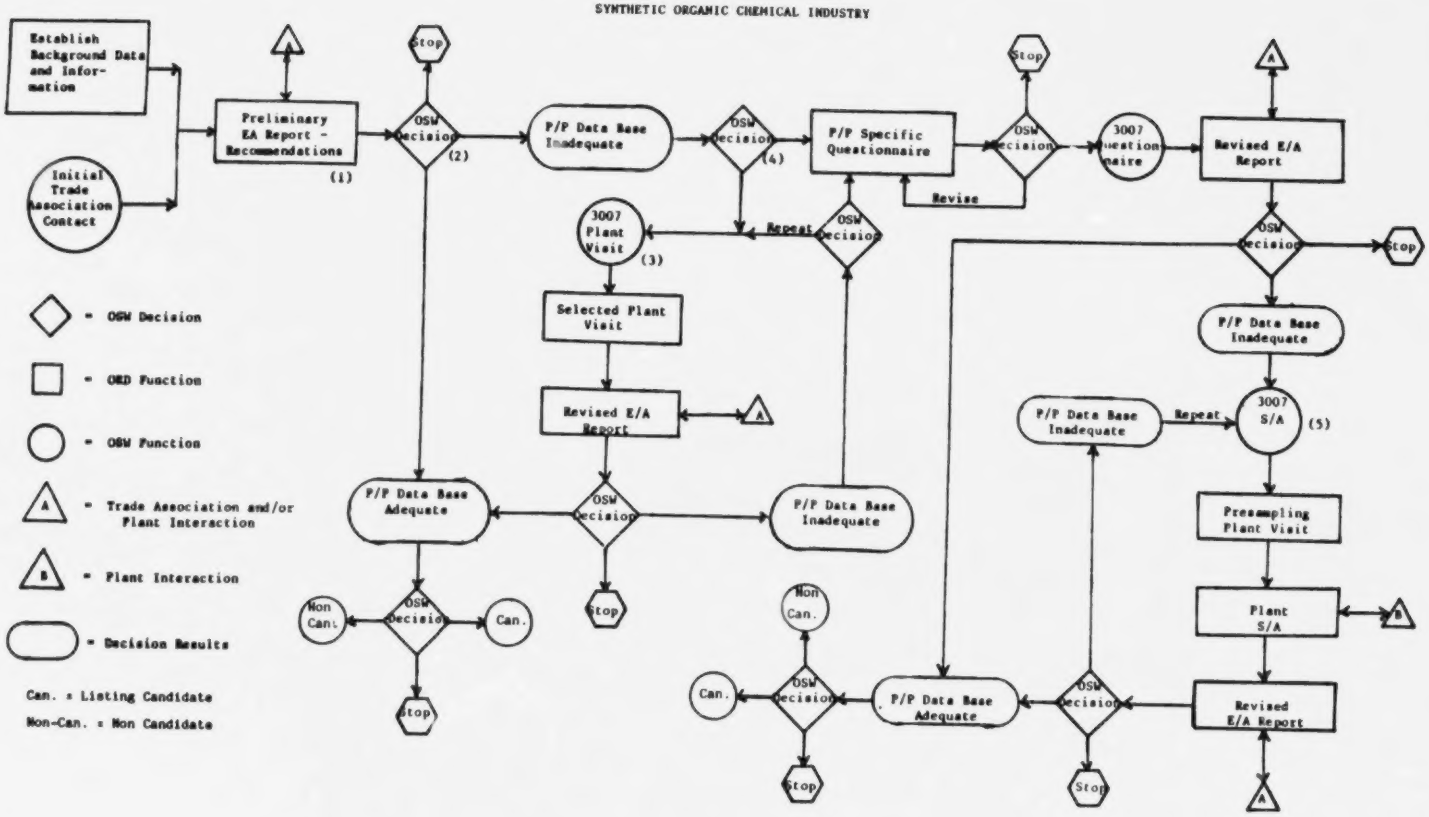
Industry	Production Chemicals (1)	Processes (#)	Companies (#)	Facilities (#)	Volume 10^6 #/yr
Basic Petrochemicals	11	28	34	107	67,000
Industrial Organics	398	600	260	544	139,000
Plastics & Resins	79	20	323	400	22,000
Synthetic Fibers	175	9	60	149	6,000
Synthetic Rubber	17	18	71	141	4,000
Plasticizers	150	3	60	78	2,000
Organic Dyes/Pigments	1,000	48	58	87	350
Pesticides	200	37	104	115	1,300
Pharmaceuticals	100	25	300	525	1
Surfactants	ND				
Specialty Organics	ND				
Flavors/Fragrances	ND				
Gum/Wood Chemicals	ND				
Fats & Oils	ND				

(1)Data comprises rough estimates based largely on 1976-7 information contained in "Industrial Process Profiles for Environmental Use"

ND = No data

Figure 1

HAZARDOUS WASTE SURVEY LOGIC
SYNTHETIC ORGANIC CHEMICAL INDUSTRY



1. Chlorinated hydrocarbons were not included since these are covered by a separate OSW study.
2. Product/processes already covered adequately by the RCRA hazardous waste listing were not included.

STATUS

As of the date of this paper, preliminary engineering analyses have been completed for most of the 35 initial product/ processes arrangements. (Table 2). These preliminary engineering analysis reports describe the industry and the production processes and identify plants that produce the subject product. (Table 3). Available data on waste streams of concern is presented in the reports.

In addition, a prototype questionnaire has been prepared for the pesticide industry segment. Based on this prototype, questionnaires tailored to each industry segment will be sent to specific plants. This information gathering is done under the provisions of Section 3007 of RCRA, which authorizes EPA to obtain data on processes and wastes pursuant to the listing process. The prototype questionnaire is currently being reviewed by OMB for approval prior to being sent by EPA to targeted industrial concerns.

A prioritized list of facilities to be visited has been prepared for each product/ process. Site visits are being scheduled. Table 4 summarizes the current program status.

The outputs from this study will be a series of background reports that will provide information to the Office of Solid Waste to be used in its decision process for listing product/processes.

TABLE 2.FIRST GROUP OF PRODUCT/PROCESSES RECOMMENDED FOR ENGINEERING ANALYSIS (TOTAL NON-AQUEOUS WASTE, Mg/yr - ITE)

(1) Propylene oxide via saponification of propylene chlorohydrin (1,550,000 Mg/yr)
(2) Epichlorohydrin via allyl chloride chlorination (179,000 Mg/yr)
(3) Glycerin via allyl chloride, hydrogenation of acrolein, and isomerization of propylene oxide (113,000 Mg/yr, 5,000 Mg/yr and 4,496 Mg/yr)
(4) Propylene oxide via peroxidation of ethylbenzene (23,000 Mg/yr)
(5) Acrylic acid and acrolein via propylene oxidation, and acrylic esters via direct esterification of acrylic acid (21,000 Mg/yr, 6,000 Mg/yr and 9,000 Mg/yr)
(6) Caprolactam via cyclohexanone (11,000 Mg/yr)
(7) Adipic acid via cyclohexanol oxidation, and cyclohexanol/cyclohexanone via cyclohexane oxidation (400,000 Mg/yr)
(8) Crude terephthalic acid via oxidation of p-xylene and dimethyl terephthalate via p-xylene oxidation and esterification (213,000 Mg/yr and 192,000 Mg/yr)
(9) Ethylene oxide/ethylene glycol via ethylene oxidation (56,000 Mg/yr and 106,000 Mg/yr)
(10) Acrylamide (all processes (1,700 Mg/yr)
(11) Bisphenol A via phenol/acetone (2,700 Mg/yr)
(12) Oxo-alcohols, including n-butyl alcohol, 2 ethylhexanol (oxo-process) (43,000 Mg/yr)
(13) Butadiene via furfural extraction and other extraction process (28,000 Mg/yr)
(14) Phenol and acetone from cumene (154,000 Mg/yr)
(15) Cumene via benzene (1,100 Mg/yr)
(16) Benzene via toluene hydroalkylation (23,000 Mg/yr)
(17) Acetic acid via butane oxidation (131,000 Mg/yr)
(18) Cyanuric chloride via HCN chlorination (128,000 Mg/yr)
(19) Hexamethylene diamine via adiponitrile and adiponitrile via butadiene (65,000 Mg/yr)
(20) Ethylamines via ethanol ammonolysis (31,000 Mg/yr)
(21) Ethyl benzene/styrene via benzene (160,000 Mg/yr and 1,900 Mg/yr)
(22) Maleic anhydride via benzene and n-butane (23,000 Mg/yr and 3,000 Mg/yr)
(23) Methyl methacrylate via acetone cyanohydrin (1,000,000 Mg/yr)
(24) Toluene diisocyanate via toluene (116,000 Mg/yr)
(25) Methylene diphenly diisocyanate via aniline condensation and phosgene via chlorination of carbon monoxide (181,000 Mg/yr and 34,000 Mg/yr)
(26) Phenol via toluene (4,343 Mg/yr)
(27) Cyclohexanol via hydrogenation of xylene (11,486 Mg/yr)
(28) Carbon disulfide (15,436 Mg/yr)
(29) Lead alkyls (726 Mg/yr)
(30) Isophthalic acid via oxidation of xylene (2,996 Mg/yr)
(31) Ethylene from natural gas and heavy liquids (307,812 Mg/yr and 205,208 Mg/yr)
(32) Methyl amine via ammonolysis of methanol (5,866 Mg/yr)
(33) Dimethyl hydrazine (4,485 Mg/yr)
(34) Ethylene diamine via ammonolysis of ethylene dichloride (2,978 Mg/yr)
(35) Acetic anhydride (5,599 Mg/yr)

TABLE 3:PRODUCT/PROCESS REPORT CONTENTS

- INDUSTRY DESCRIPTION
- PROCESS DESCRIPTION
- INTERMEDIATE PROCESS STREAMS, PROCESS WASTES, BY-PRODUCTS
- DISCUSSION ON AVAILABLE INDUSTRY INFORMATION
  - types and quantities of wastes generated
  - identification of known waste stream constituents
  - pollution control equipment
  - waste management practices

TABLE 4.STATUS OF SYNTHETIC ORGANIC CHEMICALS STUDY (3/82)

Completed

1) Development of Preliminary Engineering Analyses for 35 product/processes
2) Drafted Questionnaires for 35 product/processes
3) Evaluated Industry Responses for 2 product/processes
4) Assigned 10 additional product/processes for Engineering Analysis (12/81)

To Be Scheduled

1) Pre-sampling Plant Visits
2) Sampling and Analysis as Required

THE INDUSTRY STUDIES PROGRAM: The Organic Dyes and the Organic Pigments Industry

by

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INTRODUCTION

The Resource Conservation and Recovery Act (RCRA) of 1976, under Section 3001 requires EPA to identify and list hazardous wastes. EPA's Office of Solid Waste (OSW) is currently pursuing studies to determine which waste streams from particular production processes of organic chemicals should be listed as toxic under 40 CFR Part 261.32 of RCRA. EPA's Office of Research and Development (ORD) is providing assistance to OSW in this industry studies program. The industry segments assigned to ORD include pesticides, non-chlorinated industrial organic chemicals, dyes and pigments. This paper summarizes the approach and progress to date on the study of the organic dyes industry and the organic pigments industry being conducted by EPA's Industrial Environmental Research Laboratory in Cincinnati, Ohio (IERL-Ci).

APPROACH

The organic dye and organic pigment industries are made up of approximately 70 plants which manufacture on the order of 2000 products. Most products are of relatively low volume compared to synthetic organic chemicals (SOCMI) products, but there are indications that there may be toxic waste streams produced from these batch process operations.

The approach to this waste survey program was to delineate a group of chemical classes which included those organic dyes and pigments which are most likely to have associated wastes of concern, based on engineering judgment and existing toxicological information.

The chemical classes which have been selected include the following:

1. Azo and Azoic dyes and pigments including the subclass benzidine and benzidine congener dyes and pigments.
2. Anthraquinone dyes and pigments
3. Stilbene dyes and pigments, including fluorescent brighteners
4. Sulfur dyes and pigments
5. Phthalocyanine dyes and pigments
6. Poly-aryl methane dyes and pigments
7. Methine and polymethine dyes and pigments
8. Xanthene dyes and pigments.

It is estimated that 80% of the total production volume of organic dyes and organic pigments is covered in the Azo and Anthraquinone classes.

Selection of the number of product/processes for each class will vary with the intention of choosing a representative group.

It is very possible that the best waste candidates for listing under RCRA will exist as a result of manufacture of intermediates. Synthesis of intermediates frequently involve use of chlorinated hydrocarbon solvents which when reclaimed could yield hazardous still bottoms.

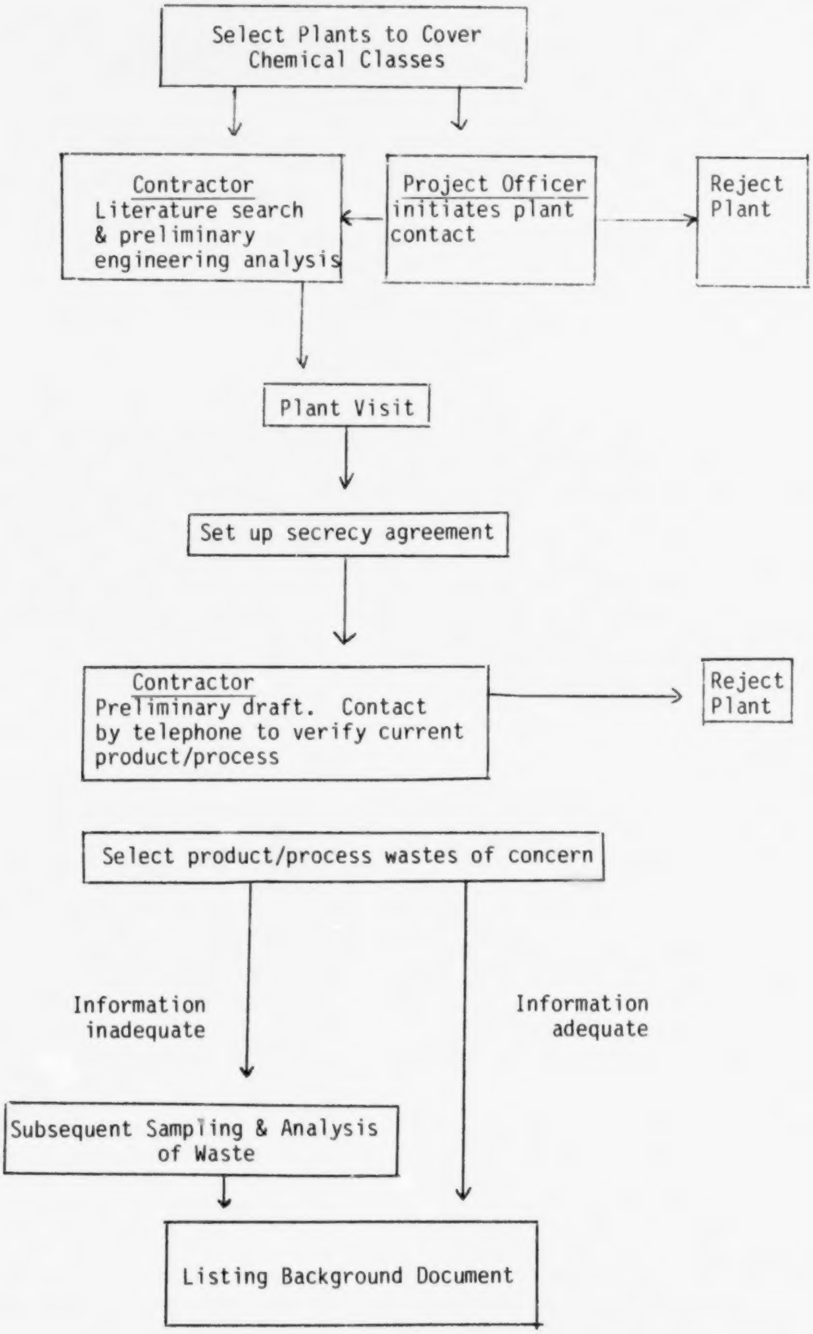
Other waste concerns involve the many amine intermediates that are toxic or are suspected carcinogens. Benzidine from benzidine dye manufacture was the first major documented occupational cancer causing problem in the chemical industry. A waste which contains significant amounts of benzidine or its congeners would be considered potentially hazardous.

CURRENT PROJECT STATUS

The waste survey program for the organic dye and the organic pigment industries is being conducted by three contractors. One of the contractors, SRI, is providing industry background documents for each of the dye and pigment chemical classes. The other contractors, TRW and GCA, are responsible for conducting the plant surveys and subsequent sampling and analyses.

TRW and GCA are now in the final stages of making initial industry contact by verifying the number and types of dyes and/or pigments produced at selected plants. Follow-up contact (e.g., site visits, questionnaires, and/or sampling and analyses) should begin early spring 1982.

FIGURE 1
Dye and Pigment Plants
Hazardous Waste Characterization Program
Logic Diagram


Select Plants to Cover Chemical Classes
Contractor
Literature search & preliminary engineering analysis
Project Officer
initiates plant contact
Reject Plant
Plant Visit
Set up secrecy agreement
Contractor
Preliminary draft. Contact by telephone to verify current product/process
Reject Plant
Select product/process wastes of concern
Information inadequate
Information adequate
Subsequent Sampling & Analysis of Waste
Listing Background Document

INCINERATION TECHNOLOGY FOR SELECTED
SMALL QUANTITY HAZARDOUS WASTE GENERATORS

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McLean, VA

ABSTRACT

The purpose of this study is to assess the application of incineration technology for destruction of small quantities of hazardous wastes generated by hospitals, universities, research stations, and related industrial sectors. The work includes characterization of the hazardous waste, geographic locations and nature of activities of generators. Quantities and applicability of available incineration technology are assessed for selected cases. A number of incinerator types were examined in the study and selected hazardous waste generators were contacted to determine their needs, problems, approaches, and experience with incineration of toxic and hazardous wastes. The generators included in this study represent a diversity of waste types as well as quantity and frequency of generation. The special problems that this diversity provides for the application of incineration are addressed in the paper.

INTRODUCTION

While small volume generators (SVG's) of hazardous wastes (with certain exceptions, those that produce less than 1000 kg/mo) are exempt from many of the provisions of RCRA, the problems they face in disposal of these wastes are similar to those faced by large volume generators. Since many SVG's depend for waste disposal on contract haulers and other outside organizations who themselves are regulated by RCRA, they still must comply with many of its requirements.

Hospitals, universities and research organizations represent a particularly challenging set of problems for hazardous waste disposal. They generate a variety of hazardous waste types from pathological and infectious wastes to inorganic and radioactive wastes. In addition the waste mix can vary substantially over a period of time depending on the nature of activities at the facility.

Increasing numbers of articles have appeared recently in newspapers concerning illegal dumping of hospital wastes and improper disposal of infectious wastes. It is not always clear from these articles whether the problem is that these wastes are placed in a proper landfill but are not properly sterilized, or that they are being dumped in improper locations. However, the use of dumps or landfills for wastes of this type does not represent an ultimate solution since the wastes have not been destroyed. On the other hand, incineration, when effective, can convert hazardous materials to innocuous forms. However, incineration is not applicable to all wastes and may not be applicable to specific facilities. The purpose of this study is to assess the application of incineration technology for destruction of small quantities of hazardous wastes generated by hospitals, universities, and research facilities.

CHARACTERIZATION OF WASTE

The wastes produced by the three types of generators under consideration generally fall into ten categories: infectious wastes, pathological wastes, carcinogens, waste pharmaceuticals, waste solvents and oils, pesticides, explosives, radioactive wastes, acids and alkalis, miscellaneous organic and inorganic chemicals. Infectious wastes are contaminated with disease-carrying agents and therefore require special handling so that they are not disseminated in the community. The moisture content and heating value varies considerably from burnable solids to infected liquid specimens. Pathological wastes, which are sometimes grouped with infectious wastes, are not specifically infectious but are subject to biological decay and may become a breeding ground for disease carriers. These wastes are generally high in moisture content and require auxiliary fuel for combustion. Carcinogens are hazardous compounds and, while many are combustible, they require special handling to prevent dispersion before combustion and they must be incinerated to a high degree of destruction. Carcinogens are generated in relatively small quantities. Waste pharmaceuticals which are more likely to be generated by pharmaceutical industries than by the subject SIC's, are generated by hospitals in small quantities and consist of drug residues and waste pills and capsules. Controlled substances may be subject to special accountability. Solvents and oils are generally flammable liquids consisting of hydrocarbons, chlorinated hydrocarbons, and sulfur-containing solvents. The value of these materials makes them attractive for recovery and reuse if the waste mixture does not contain too many components. Waste pesticides are usually generated in low volume or consist of spent containers. These are generally organic materials and include chlorinated hydrocarbons and phosphorus compounds. These are incinerable in special equipment with flue gas scrubbing but are generally not recommended for incineration in standard equipment. Explosives likewise are incinerable in special equipment, but handling and cleanup requirements make these generally unattractive for incineration. Radioactive wastes are controlled by special licensing procedures and will not be addressed here. While many low-level radioactive wastes are incinerable, the incineration process does not change the radioactivity of the substances, and special handling and effluent controls would be required. Acids and alkalis are generally liquid wastes that are corrosive and poisonous. They are most easily handled by neutralization and are not generally amenable to incineration. A wide variety of other organic and inorganic substances may be generated at research facilities depending on the specific nature of ongoing research.

GENERATION OF WASTE

The applicability of incineration may depend not only on the characteristics of the waste generated but also on the quantities and frequency of waste generation and, to a certain extent, on geographic location. The generation of consistently large quantities of combustible hazardous waste makes on-site incineration more attractive provided local regulations can be met.

Only limited data are available on the quantity and frequency of waste generation and the data base is not sufficient to provide precise quantitative information. However, it appears that qualitative and directional information can be derived from the data. The information below was drawn primarily from Reference 1 with cross-checks from a number of facility contacts made under this study. While in some cases the number of establishments contacted in this study exceeded the number on which the statistics in Reference 1 were based, the information was generally in qualitative agreement.

For the purposes of this study, small volume generators are those which produce less than 1000 kg/mo of hazardous waste. While RCRA controls certain substances at lower generation rates, the 1000 kg/mo value was used to examine the generation data base. To put things in perspective for the three types of waste generators under consideration, SIC 28-Chemicals and Allied Products produces a total lf 1500 x 10^6 kg/mo of hazardous waste. Small volume generators within SIC 28 (those producing less than 1000 kg/mo produce a total of 4.5 x 10^6 kg/mo.

Small volume generators in the subject SIC codes produce the following quantities of hazardous waste:

- SIC 806 - Hospitals
  0.8 x 10^6 kg/mo
- SIC 8071 - Medical Laboratories

0.3 x 10^6 kg/mo
- SIC 822 - Colleges, Universities, Professional Schools, and Junior Colleges
  0.2 x 10^6 kg/mo
- SIC 892 - Noncommercial Educational, Scientific, and Research Organizations
  0.05 x 10^6 kg/mo
- SIC 7391 - Research and Development Laboratories
  0.3 x 10^6 kg/mo
- SIC 7397 - Commercial Testing Laboratories
  0.3 x 10^6 kg/mo

It is important to emphasize that the above numbers are based on limited data but are probably directionally correct.

Census data were used in Reference 1 to provide a breakdown by SIC code of the number of facilities in each EPA region. Using the assumption that small volume generators are distributed geographically the same way as all generators within the SIC code, Table 1 provides an approximate distribution of small volume generators in the subject SIC codes.

Using the above numbers for total quantities of hazardous wastes generated by small volume generators and the total number of small volume generators, Table 2 provides an idea of the average rate of hazardous waste generation and the relationship of small volume generators to all generators in the SIC.

CURRENT WASTE MANAGEMENT PRACTICES

Methods by which each of the waste categories mentioned in a previous section are managed by small and large volume generators will be discussed briefly. For the most part there are few differences in the types of management practices used by small and large generators, but economy of scale will favor one management technique over another. In general, economics will determine the specific choice from among those available.

Infectious and pathological wastes are generally treated by one of three methods. They are usually disinfected by autoclaving, or chemical treatment, or incineration, and the residue is contract hauled or disposed of as normal trash. Waste drugs are generally incinerated on-site, returned to the manufacturer, diluted to the sewer or sent to a drug enforcement agency. Oils and solvents are generally sent to a recycler, treated for reuse on-site, drummed and contract hauled, or burned in a boiler or an incinerator. Waste pesticide liquids are generally drummed and contract hauled. Empty containers are generally rinsed to the ground or the sewer and the rinsed containers are disposed in the normal trash. Acids and alkalis are generally neutralized and diluted to the sewer.

The wastes that are most amenable to incineration from the above are infectious and pathological wastes, some waste pharmaceuticals, waste solvents and oils, and miscellaneous organic chemicals. Decisions on the most suitable method for disposal will be made on site-specific and economic bases.

Other methods that may help reduce the ultimate amount of hazardous materials discarded have been suggested. Management controls on procurement policy to discourage the ordering of surplus chemicals and to encourage recycling of chemicals may make a contribution to reducing the amount of waste but will not completely solve the disposal problems. (2)

Contract hauling handles many problems for the waste generator including responsibility for disposal and legal and regulatory requirements. However, the waste generator may still be liable if the contract hauler disposes of the hazardous material improperly. For some wastes contract hauling is the only viable solution.

Incineration, if applicable and effective, provides an ultimate solution to the waste disposal problem. As opposed to land disposal where the hazardous material still have the potential to create environmental problems, incineration converts the hazardous material into an innocuous form. Unfortunately, especially for small volume generators, there are operational, energy and economic problems that may limit its usefulness.

APPLICABILITY OF INCINERATOR TECHNOLOGY

Since the current study is still in progress, it is premature to draw final conclusions, but a number of incinerator types have been examined and selected hazardous waste generators have been contacted to determine their needs, problems, approaches, and experience with incineration of toxic and hazardous wastes. Some of the salient points will be summarized in this section.

Thirty-nine incinerator manufacturers were contacted to obtain information on the availability of incinerators for destruction of hazardous wastes from small volume generators. Units with capacities as low as 11 kg/hr were found. As waste generators were contacted about their experience, additional incinerator manufacturers were identified. The approaches varied widely from manufacturer to manufacturer. The most highly developed hazardous waste incineration technology is represented by rotary kiln and liquid injection incinerators. Fluidized bed and multiple hearth incinerators are also commercially available. A number of innovative and emerging technologies, including starved air combustion/pyrolysis, molten salt incineration, molten glass incineration and plasma arc pyrolysis have also been put into use. The assessment of incinerators has not been completed at the time of writing. Descriptions of the more common types of incinerators, their status, wastes handled, advantages and disadvantages may be found in EPA's Engineering Handbook for Hazardous Waste Incineration. (3)

A recent paper from the National Institutes of Health (2) reported on a screening study of five incinerators for their general suitability for destruction of hazardous organic chemicals. Five units were tested 1) a two-chamber refractory-lined incinerator, 2) a three-chamber, vertically-aligned incinerator, 3) a dual-chamber, rectangular incinerator, 4) a dual-chamber, refractory-lined, batch incinerator, 5) a molten salt catalytic incinerator. An organic chemical tracer was used to monitor the effectiveness of destruction of common organic chemicals and a fire retardant chemical was used to monitor the effectiveness of combustion. In addition, hydrocarbons, nitrogen oxides, hydrogen chloride, sulfur oxides, and particulates were monitored. As indicated in Table 3, all units demonstrated relatively good performance although Unit 5 had some problems with hydrocarbons and particulates, possibly caused by short-duration smoke emissions after charging.

Incineration offers significant advantages in disposing of wastes consisting primarily of organic materials with high heating values. Unlikely candidates for incineration are heavy metals, high-moisture content waste, inert material, inorganic salts, and material with high inorganic content. A number of small volume generators already make use of incineration for wastes not currently regulated by RCRA and it appears that a number of units show promise for waste disposal at hospitals, universities and research facilities. While RCRA does not require trial burns for small volume generators disposing of hazardous wastes by incineration, many want assurance that a particular incinerator can achieve a destruction/removal efficiency of 99.99% with their mix of wastes.

REFERENCES

1. Ghassemi, M., et al 1979. Technical Environmental Impacts of Various Approaches for Regulating Small Volume Hazardous Waste Generators. Final Report, Contract 68-02-2613 Work Assignment 27 and Contract 68-03-2560 Work Directives T-5012, T-5014, and T-5015, U.S. Environmental Protection Agency, Washington, D.C.

2. Rogers, H.W. 1979. Hazardous Wastes-New Developments. J. American College Health Association 28: 158-164.

3. Bonner, T. et al 1980. Engineering Handbook for Hazardous Waste Incineration. Draft Final Report, Contract 68-03-2550 Work Directive T1016, U.S. Environmental Protection Agency, Cincinnati, OH.

TABLE 1. APPROXIMATE GEOGRAPHIC DISTRIBUTION OF SMALL VOLUME GENERATORS IN SUBJECT SIC CODES

	Number of Small Volume Generators*										
		EPA Region									
SIC Code	Nation	I	II	III	IV	V	VI	VII	VIII	IX	X
806 Hospitals	6814	450	579	743	1015	1240	859	477	361	852	238
8071 Medical Labs	3876	220	430	291	445	744	508	151	89	841	155
822 Universities	1807	162	237	258	266	340	114	125	42	202	56
892 Non commercial Educational Scientific & Research	1075	Not Available									
7391 R&D Labs	1461	165	197	190	124	213	127	39	61	295	47
7397 Testing Labs	1285	69	130	107	190	222	215	49	60	194	48

*Based on data in Reference 1 and assuming a geographic distribution for small volume generators similar to that for all generators. Individual numbers are approximate.

TABLE 2. WASTE GENERATION BY SELECTED SMALL VOLUME GENERATORS*

SIC CODE	Total Number Of SVG's	Total Waste From SVG's (kg/mo)	Average Rate of Generation by SVG's (kg/mo)	SVG's As Percent Of Facilities in SIC	SVG Waste As Percent of Total Waste in SIC
806 Hospitals	6814	0.8×10^6	120	92	27
8071 Medical Labs	3876	0.3×10^6	70	99	73
822 Universities	1807	0.2×10^6	120	87	33
892 Noncommercial Educational Scientific & Research	1075	0.05×10^6	50	92	21
7391 R&D Labs	1461	0.3×10^6	230	73	11
7397 Testing Labs	1285	0.3×10^6	220	94	62

*Calculated from data in Reference 1

TABLE 3. RESULTS OF INCINERATION TESTS IN REFERENCE 2

Incinerator	Hydrocarbons (ppm)	NO_x (ppm)	HCl (ppm)	SO_x (ppm)	Particulate GR/cu.ft.
Unit 1	9.1	12.7	BD* (<4.7)	45.8	0.0425
Unit 2	11.2	24.3	7.8	20.2	0.0120
Unit 3	7.1	29.4	BD (<2.4)	103.2	0.2452
Unit 4	No Data	24.4	32.5	30.0	0.0467
Unit 5	72.6	14.2	BD (<2.4)	24.8	0.1552

*BD - Below detectable limit

HAZARDOUS WASTE CONTROL TECHNOLOGY DATA BASE

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This paper describes the program to develop an automated data base storing technical information on the thermal destruction of hazardous wastes. The data base will store detailed design, operating, and performance data obtained from incineration facility permit applications, trial burn reports, research and development projects, and contractor data gathering efforts. The paper describes the development process itself and presents some of the details of the system as it will be implemented, including descriptions of the data content and structure, and input and retrieval features.

INTRODUCTION

Incineration has long been an important technique for the destruction of hazardous waste. Recently, however, especially since the passage of the Resource Conservation and Recovery Act (RCRA), incineration practices have begun a period of rapid advances in technical sophistication and complexity. Many new systems are evolving using a diverse group of thermal destruction concepts and designs.

As required by RCRA, EPA is developing a regulatory program addressing the incineration of hazardous wastes. In order to insure that this program is developed and implemented with the benefit of the most current industry experience with advanced incineration techniques, there is a need for EPA to obtain and analyze technical design and operating data from both existing incineration facilities and research activities in this area.

As part of its support to the Office of Solid Waste, the Incineration Research Branch (IRB) of the Industrial Environmental Research Laboratory in Cincinnati has a multi-faceted program underway to develop such a data base, which will be called the Hazardous Waste Control Technology Data Base (HWCTDB). The objectives of this data base are:

- to provide direct technical support to Regional permit and compliance programs, especially in the evaluation of requests for trial burn exemptions;
- to form a sound technical basis for development and promulgation of future revisions of regulations for hazardous waste incinerators;
- to define the range of current engineering practice, particularly regarding the performance associated with various design and operating characteristics;
- to provide a foundation on which to plan future R&D efforts addressing thermal destruction of hazardous wastes.

The data base will store detailed technical design, operating, and performance data obtained from incineration facility permit applications, trial burn reports, research and development projects, and contractor data gathering efforts. Specific data content was chosen based on a user needs study conducted early in 1981 (Barrett, et. al., 1981), and on the information requirements for permit evaluation as identified in the "Guidance Manual for Evaluating Permit Applications for the Operation of Hazardous Waste Incinerator Units" (Vogel, et. al., 1981).

This paper describes the program to develop the data base as well as some of the details of the system as it will be implemented. Since the system will not be completed until early 1982, several months after preparation of this paper, some of the details described here may be modified slightly in the operational system. The program to develop this data base consists of three major phases, as described below: initial development, implementaion, and system operation.

INITIAL DEVELOPMENT

The initial development phase was completed by the MITRE Corporation this summer. It consisted of a user needs survey to identify user requirements for both content of and access to the data base, a review of existing data bases for potential implementation of the HWCTDB, and the development of an initial list and description of desired data elements.

The user needs study identified sixteen organizations within EPA and DOE as potential users of the data base. Discussions with various members of each organization indicated a need for obtaining a wide range of data on both administrative and technical features of incineration facilities, as well as other types of facilities destroying hazardous wastes. Further, a strong preference was expressed for on-line retrievals and the ability to sort by many different criteria, including various waste characteristics and a range of incineration design and operating features.

To minimize the time and effort required for system development and user training, and to maximize standardization of EPA's information systems, an effort was made to identify an existing data base which could be easily adapted to meet the needs defined above (Dratch and Keitz, 1981). A review of EPA's System Information Directory (US EPA, 1980) revealed seven potentially applicable data bases.

Further analysis narrowed the consideration to two systems: the Hazardous Waste Data Management System (HWDMS), operating for OSW, and the Environmental Assessment Data Systems (EADS), managed by ORD. Both utilize Intel Systems Corporation's System 2000 Data Base Management System to organize their data. Analysis of the two systems indicated that each could be adapted to meet the needs of HWCTDB. EADS is well suited to storage of source characterization and emissions test data, but would still require special programs to obtain many of the common sorting and retrieval capabilities desired by users. HWDMS is designed to store and organize information received in applications for hazardous waste facility permits. Current plans are to expand the data base in phase with OSW's permit program to eventually include the data received on Part B applications.* HWDMS, therefore, already contains the administrative information desired by users and would eventually contain much of the technical design and operating data required on Part B facility permit applications. Further HWDMS is already familiar to and used by OSW (who will be one of the major users of HWCTDB), has a user-support group in the EPA Regional Offices, and has a more versatile data input system to facilitate data entry and validation. The planned expansion of HWDMS would also provide the opportunity to build the desired capabilities into the primary structure of the data base. Therefore, a recommendation was made to build HWCTDB as an expansion of HWDMS.

The final portion of the initial development phase was the construction of a preliminary data dictionary describing the desired data elements and their relation to each other (Holberger, 1981). A total of 155 data elements, grouped into 22 record groups (repeating groups) were identified. This effort also included specification of some of the reports and retrievals which would be requested from the system.

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*The application process for obtaining a hazardous waste facility permit occurs in two stages. The Part A application requires administrative information and a general description of the facility. It is the basis EPA uses for granting interim status. The Part B application will contain the detailed technical data necessary for EPA's evaluation of the ability of the facility to meet the requirements for a full hazardous waste facility permit.

IMPLEMENTATION PHASE

The Implementation Phase consists of three parts: systems development and documentation, data collection, and acceptance testing (which includes the initial data loading). Both the systems development and data collection portions are underway as of this writing.

Systems Development and Documentation

This effort includes the finalization of the system requirements; system design, systems programming, documentation and user training. (Documentation and user training activities will also extend into the system operation phase.) The final system design, the systems programming, and the software-related portions of the documentation and user training will be prepared by the Computer Sciences Corporation (CSC), based on the system requirements specified by EPA and MITRE. As of this writing, the data dictionary is being completed with the addition of edit criteria and specification of required data for input to the data base; a preliminary system design is being prepared for final review; CRT screen formats are being developed for data entry; and final report formats and retrieval criteria are being prepared.

Figure 1 shows the structure and content of the data base as of this writing. Final implementation may differ slightly. At present, there are 159 data elements in 21 records (repeating groups).* The primary record under which the others are organized is the C0, or Facility Record. It contains much of the administrative data presently existing in HWDMS. Each facility would have one Facility Record. All other records would be considered descendants of the Facility Record, and may occur many times for each facility. For example, a given facility may burn more than one waste, and each waste will contain numerous constituents, some of which will be designated as Principle Organic Hazardous Constituents (POHC's). Therefore, the name of each constituent analyzed in the waste, its concentration in the waste, and a flag indicating its status as a POHC would comprise a separate Waste Composition Record (C2840) descending from the Waste Characterization Record (C1800) organizing the complete description of that waste. Each group of records describing a single waste stream (consisting of one C1800 record and all its descendants) would be a separate repeating group descending from the Facility Record (C0).

As designed, the HWCTDB will store information on multiple units at each facility, each with multiple sets of operating conditions. Separate descriptions of design and operating conditions will be maintained for each chamber of multiple chamber facilities, and many separate waste streams may be associated with each chamber. Since the Waste Characterization Record is not a descendant of the Operating Conditions Record Group, data may be stored describing the destruction of the same waste stream under many different operating conditions or designs without repeating the waste description. The use of comments describing distinctive characteristics of any portion of the facility or its operations is encouraged, with comment numbers designed to indicate the subject of each comment.

The system programming and CSC's internal testing will be conducted during the winter of 1981-1982, with a planned turnover date in early spring 1982. The programming effort will involve actual construction of the data base, programs to load information from and maintain consistancy with HWDMS permit data, programs for report generation, and the provisions for a few special retrievals expected to be too complicated for most users.

Documentation of the data base will include preparation of a System Management Summary, System User's Guide, System Maintenance and Operations Manual and Technical User's Guide. The first three documents will address the system-oriented procedures for manipulating and maintaining the data base. The fourth document will address the non-computer oriented user community, providing descriptions of methods to maximize utility of the data base to support both regulators and researchers. User-training sessions will proceed in parallel with the documentation.

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*In this discussion, a record or repeating group is defined as a group of related data elements describing one particular aspect of a facility and its operations. Each record and each data element has been assigned a reference number prefixed by the letter C.

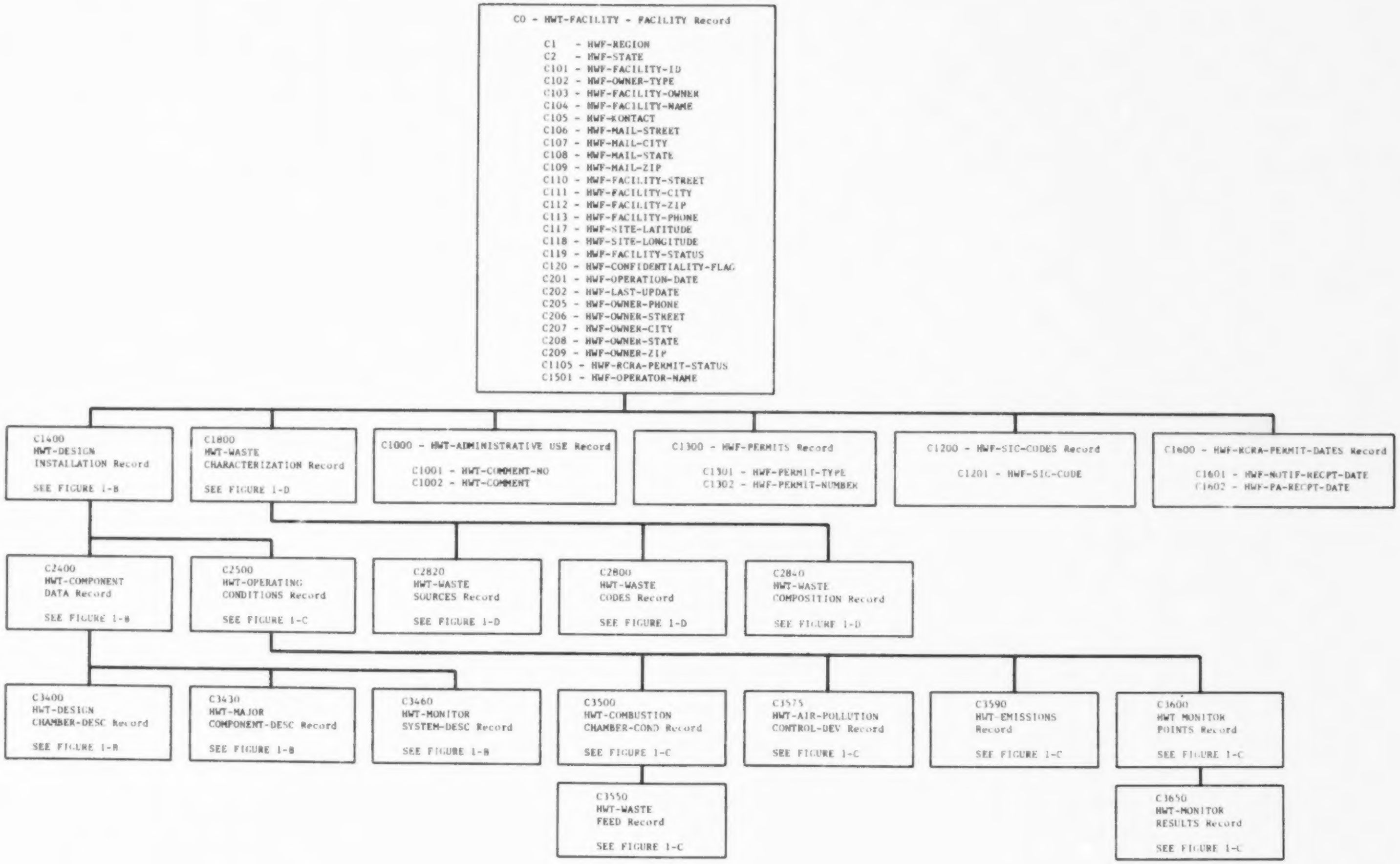
CO - HWT-FACILITY - FACILITY Record
C1 - HWF-REGION
C2 - HWF-STATE
C101 - HWF-FACILITY-ID
C102 - HWF-OWNER-TYPE
C103 - HWF-FACILITY-OWNER
C104 - HWF-FACILITY-NAME
C105 - HWF-KONTACT
C106 - HWF-MAIL-STREET
C107 - HWF-MAIL-CITY
C108 - HWF-MAIL-STATE
C109 - HWF-MAIL-ZIP
C110 - HWF-FACILITY-STREET
C111 - HWF-FACILITY-CITY
C112 - HWF-FACILITY-ZIP
C113 - HWF-FACILITY-PHONE
C117 - HWF-SITE-LATITUDE
C118 - HWF-SITE-LONGITUDE
C119 - HWF-FACILITY-STATUS
C120 - HWF-CONFIDENTIALITY-FLAG
C201 - HWF-OPERATION-DATE
C202 - HWF-LAST-UPDATE
C205 - HWF-OWNER-PHONE
C206 - HWF-OWNER-STREET
C207 - HWF-OWNER-CITY
C208 - HWF-OWNER-STATE
C209 - HWF-OWNER-ZIP
C1105 - HWF-RCRA-PERMIT-STATUS
C1501 - HWF-OPERATOR-NAME
C1400 HWT-DESIGN INSTALLATION Record SEE FIGURE 1-B
C1800 HWT-WASTE CHARACTERIZATION Record SEE FIGURE 1-D
C1000 - HWT-ADMINISTRATIVE USE Record
C1001 - HWT-COMMENT-NO
C1002 - HWT-COMMENT
C1300 - HWF-PERMITS Record
C1301 - HWF-PERMIT-TYPE
C1302 - HWF-PERMIT-NUMBER
C1200 - HWF-SIC-CODES Record
C1201 - HWF-SIC-CODE
C1600 - HWF-RCRA-PERMIT-DATES Record
C1601 - HWF-NOTIF-RECPT-DATE
C1602 - HWF-PA-RECPT-DATE
C2400 HWT-COMPONENT DATA Record SEE FIGURE 1-B
C2500 HWT-OPERATING CONDITIONS Record SEE FIGURE 1-C
C2820 HWT-WASTE SOURCES Record SEE FIGURE 1-D
C2800 HWT-WASTE CODES Record SEE FIGURE 1-D
C2840 HWT-WASTE COMPOSITION Record SEE FIGURE 1-D
C3400 HWT-DESIGN CHAMBER-DESC Record SEE FIGURE 1-B
C3430 HWT-MAJOR COMPONENT-DESC Record SEE FIGURE 1-B
C3460 HWT-MONITOR SYSTEM-DESC Record SEE FIGURE 1-B
C3500 HWT-COMBUSTION CHAMBER-COND Record SEE FIGURE 1-C
C3550 HWT-WASTE FEED Record SEE FIGURE 1-C
C3575 HWT-AIR-POLLUTION CONTROL-DEV Record SEE FIGURE 1-C
C3590 HWT-EMISSIONS Record SEE FIGURE 1-C
C3600 HWT MONITOR POINTS Record SEE FIGURE 1-C
C3650 HWT-MONITOR RESULTS Record SEE FIGURE 1-C

FIGURE 1-A
HAZARDOUS WASTE CONTROL TECHNOLOGY DATA BASE

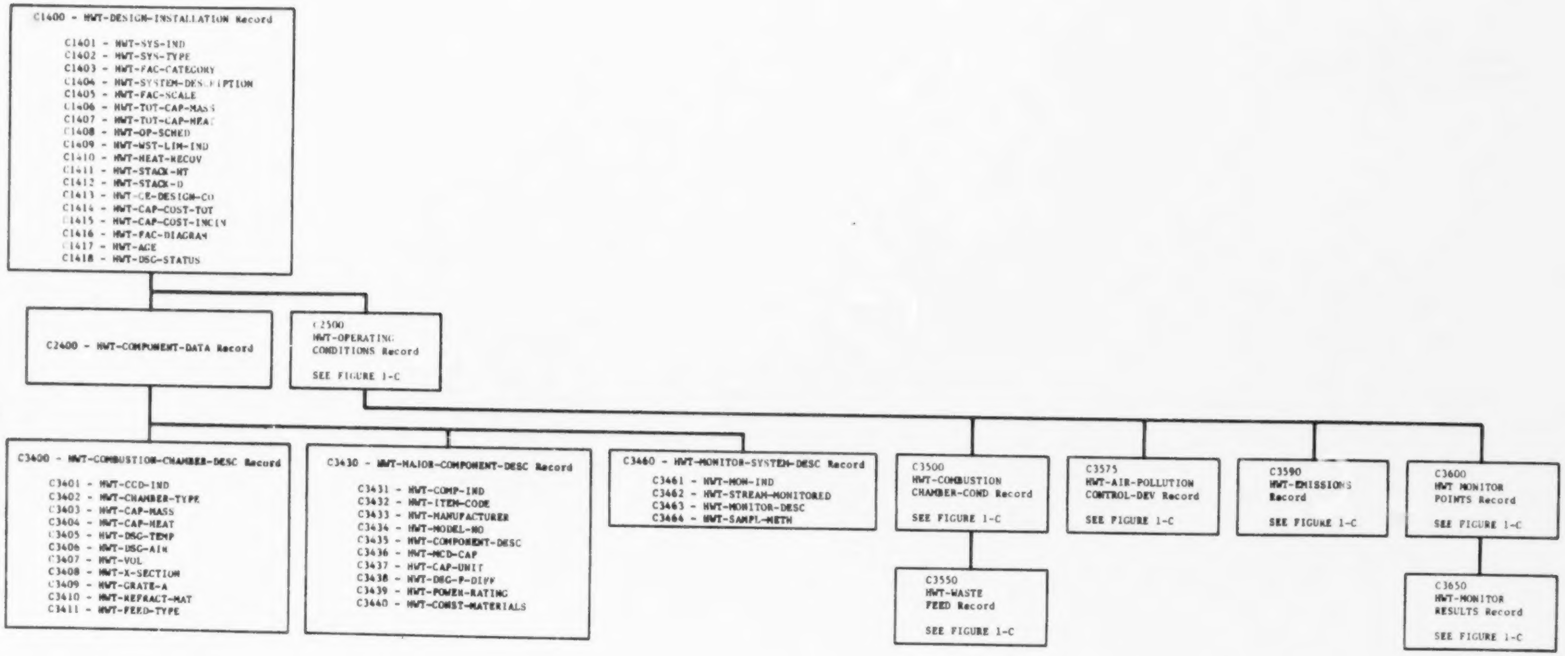

FIGURE 1-B
HAZARDOUS WASTE CONTROL
TECHNOLOGY DATA BASE
(CONTINUED)

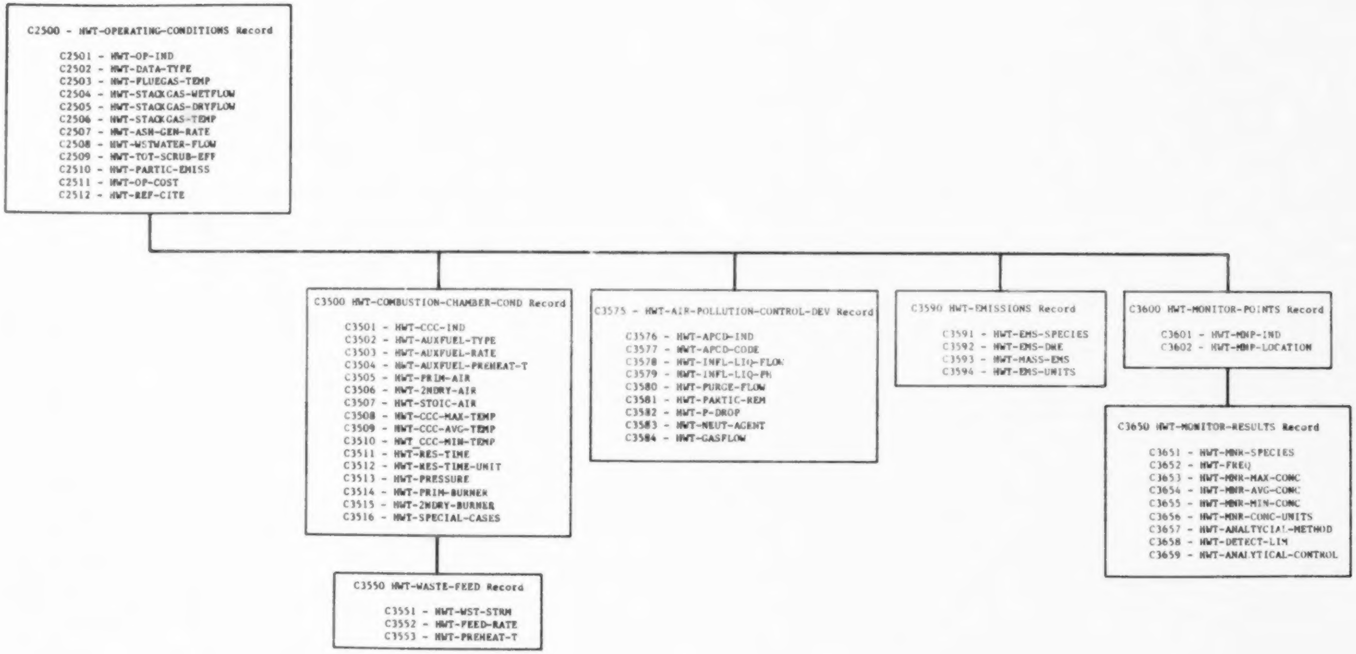

FIGURE 1-C
HAZARDOUS WASTE CONTROL
TECHNOLOGY DATA BASE
(CONTINUED)

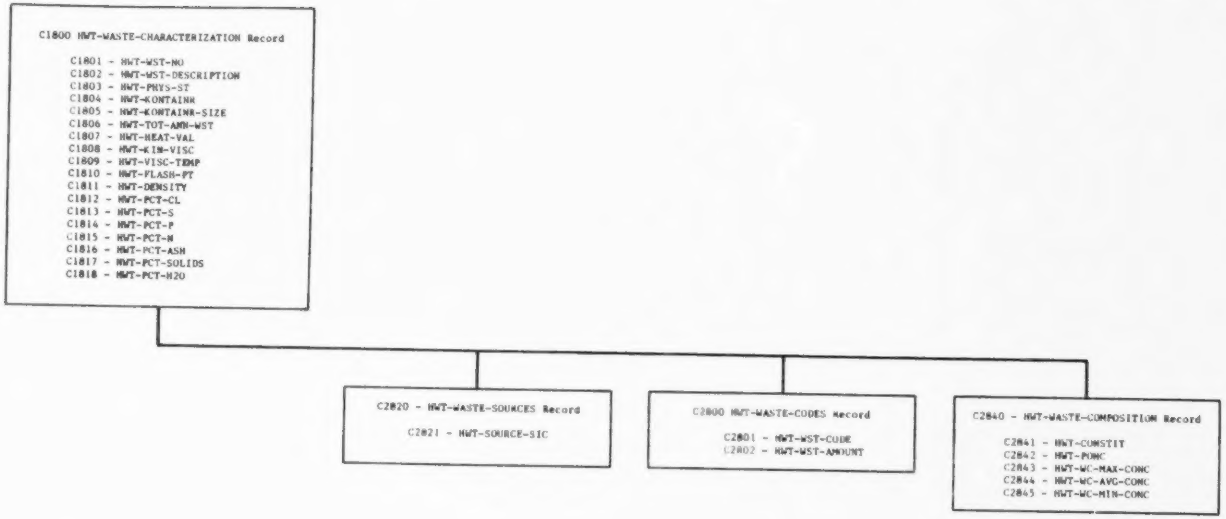

FIGURE 1-D
HAZARDOUS WASTE CONTROL
TECHNOLOGY DATA BASE
(CONCLUDED)

Data Collection

The second part of the implementation phase is data collection. The MITRE Corporation has completed a task to obtain data from manufacturers of incineration systems, documented in "Profile of the Hazardous Waste Incinerator Manufacturing Industry" (Frankel, et. al., 1981). Under a separate task, MITRE has also begun collecting information from operating incineration facilities. Data is collected through telephone and personal interviews with facility operators who have submitted RCRA permit applications. Data collected during this and subsequent tasks will be recorded on data entry forms designed to correspond to the CRT screens used during data entry to the system.

Incorporation of this data into the automated data base will not occur until the acceptance tests are underway. After the initial loading of the data base, data will be input to the system using full screen CRT terminals connected to EPA's PDP-11/70 minicomputers. Figure 2 is an example of one of the screens which will be used to input data for the Major Component Description Record (C3430). The first two lines identify the facility and design records to which the data applies. The screen then contains a list of the elements in the record, along with blanks sized for the maximum length of each element. The cursor will automatically move from one field to the next, allowing inputs only in the appropriate positions. As each data element is entered, the edit program will check to ensure that it is a valid entry.

The edit procedure is a series of computer programs which check that each entry fits the description for the appropriate data element (i.e., correct type - decimal, integer, or alphanumeric; and correct number of characters) and that the entry has a valid value (some of the data elements, such as the Item Code, are restricted to certain sets of common terms or codes; other numeric data have valid ranges, outside of which they will not be accepted by the data base, e.g., no combustion temperatures will be allowed outside the range 500-4000°F). If the screen entry does not pass the edit test, the program will print an error message and give the operator the opportunity to correct it immediately. After data for each element has been entered on the screen, the program will give the operator another opportunity to correct any errors not detected by the edit program.

After completing the entries for one major incineration system component (e.g., for the description of the waste feed system), the operator may then request another repetition of the screen for entry of an additional record (e.g., for the description of a venturi scrubber), or may request the screen for a different record group (e.g., for the data elements comprising the Monitor System Description Record (C3460). When the data meets the approval of both the operator and the edit procedure, the program will construct an update file for later entry on the full data base, which will physically reside in EPA's IBM 370 in Research Triangle Park.

Acceptance Testing

The final portion of the implementation phase is the acceptance testing and system initialization, which will begin as CSC completes the system programming and "turns over" the software to EPA. The testing procedure will exercise each system function (data entry, edits, update, retrieval, etc.) with both valid and invalid "dummy" data. System performance will also be evaluated relative to the design requirements. Any deficiencies will be noted for correction. All data introduced during the acceptance test will be deleted after successful completion of the test procedure.

System initialization and performance testing will begin with the initial loading of "live" data on the data base, including both the conversion of data from the HWDMS and the entry of data collected up to that time. System performance and integrity will be monitored closely for several months to detect previously undiscovered problems. This effort will be coordinated with user-training activities and the establishment of procedures for use of the data base by ORD and Regional EPA personnel.

SYSTEM OPERATION

The system operation phase of this project includes completion of documentation and user training efforts and continuation of data collection and entry as described above, long term data base

FIGURE 2

MAJOR EQUIPMENT DESCRIPTION
SCREEN 3430

```
FACILITY ID ___________      FACILITY _____________________________________________
SYSTEM INDEX ____            SYSTEM TYPE ____

TYPE 'Y' IF THIS IS A NEW EQUIPMENT ITEM FOR THE FACILITY ___

COMPONENT INDEX ____                                ITEM CODE ____
MANUFACTURER______________________________          MODEL # ___________________________
CAPACITY__________     UNITS__________
DESIGN PRESSURE CHANGE ______ IN H2O                POWER RATING ____HP

MATERIALS ________________________________________

DESCRIPTION
___________________________________________________________________________________
___________________________________________________________________________________

TO ADD COMMENTS TYPE 'Y' *

TYPE 'R' TO REPEAT THE MAJOR EQUIPMENT DESCRIPTION SCREEN *
TYPE 'M' TO GO BACK TO THE DESIGN DESCENDANT MENU *
ERROR MESSAGES
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management and maintenance, data base utilization, and continued system evaluation and enhancement (as required).

Long term management and maintenance will involve designating a data base administrator (DBA) who will be responsible for access to the data base, data integrity, file maintenance, backup and recovery procedures, periodic reconciliation with HWDMS, and monitoring the continued development and use of the data base. The DBA will also control the data entry process, taking the update files created by the edit programs and incorporating them in the data base.

A user support group will be established to provide a retrieval service for any users requiring assistance. This group will maintain a library of special retrieval programs of general interest to the user community, provide assistance in formulating retrieval requests and interpreting outputs, and will operate an online news service to keep users informed on new retrievals or other items of interest pertaining to the data base. The user support group will also coordinate the creation and distribution of additional documentation and the training of new users, as necessary.

The system is being designed so that many of the common retrievals may be performed quickly in interactive terminal sessions using System 2000's Natural Language. To perform such retrievals, the user requires knowledge of the data base logical structure (Figure 1), and usually needs to attend a short user-training course to learn the concepts of Natural Language. No other computer-related experience will be required for simple retrievals.

The basic retrieval procedures will involve using Natural Language to identify facilities with certain combinations of characteristics (e.g., commercial liquid injection units operating under starved air conditions within a certain temperature range). After identifying the facility identification number (element C101) and any other information needed to uniquely identify the records meeting the selection criteria (e.g., waste sequence number or system index), the user may choose one or a combination of several output report formats. A list of the standard reports and a summary of their contents is presented in Table 1. A user may augment the reports by requesting additional data elements, depending on his needs.

The final aspects of the system operational phase are continued evaluation and enhancement, which include on-going evaluation of system performance with respect to both the original objectives and to the continued evolution of EPA's programs. An annual assessment will be prepared to document the current system performance, identify new program needs which could be met by the data base, and suggest enhancements which would increase the utility of the data base or improve procedures identified by users as cumbersome. Recommended enhancements could include the development of additional retrieval capabilities and new reports, modifications to the data content or structure of the data base, or simple expansion of the supporting documentation.

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TABLE 1

STANDARD REPORTS FROM HWCTDB

REPORT	CONTENTS
Basic Identification Package	Facility name, location, identification number and permit status.
Expanded Identification Package	Contact name and phone, owner name, mailing address.
Waste Stream	Waste sequence number, description and selected elements from the Waste Characterization record and its descendants
Incinerator Design	System index, System type, and description, and other selected elements from the Design-Installation record and Component Data record and its descendants.
Operating Conditions	Operating conditions index, data type and other selected elements from the Operating Conditions record, Combustion Chamber record, Waste Feed record and Air Pollution Control Device record.
Performance	Operating conditions index, data type, total scrubber efficiency, particulate emissions, and all Emissions records containing a value for DRE.
Monitor Results	List all monitor records for a specified monitor (given a facility ID, system index, and operating conditions index).

TABLE 1

(Continued)

REPORT	CONTENTS
Burn Summary	Extracts selected data elements from the Facility record, Waste Characterization record, Design/Installation record, Component Data record and Operating Conditions record, providing a summary of the type of waste burned, type of system used, operating conditions used, and resulting emissions.
Data Base Summary	Provides total of certain values, (e.g., total liquid injection capacity); ranges of values (e.g., range of temperatures used in rotary kilns); or counts of the number of occurrences of certain values (e.g., number of units combining rotary kiln and liquid injection).

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OVERVIEW OF THE CONCEPT OF DISPOSING OF HAZARDOUS WASTE IN INDUSTRIAL BOILERS

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ABSTRACT

This Paper discusses the results of the first phase of an overall study in which the technical feasibility of the concept of disposing of hazardous waste by co-combusting it with conventional fuels in industrial boilers is examined. The second phase of the study involves the generation of appropriate sampling and analysis protocols and the conduct of an investigation to locate candidate industrial boiler testing sites. Phase three, just now getting into full swing, involves an actual Testing Program to determine the effectiveness of destroying hazardous wastes by co-firing them in industrial boilers.

In this Paper, the estimated quantities of hazardous wastes generated each year are discussed, as are the projections of the number of industrial boilers currently in operation. A kinetic model for the thermal destruction process that takes place in a boiler is described. Waste decomposition rate curves are compared to boiler temperature/residence time curves to allow prediction of the waste's destructibility in a given industrial boiler. The kinetic model is applied to a real-life PCB test burn situation and the prediction-versus-reality is compared.

INTRODUCTION

It has been estimated that approximately 41 million metric tons of hazardous wastes are generated each year in the United States (2,9). The environmentally acceptable disposal of these hazardous wastes is a mandated goal of the Resource Conservation and Recovery Act (RCRA). Regulations proposed and promulgated by the U.S. Environmental Protection Agency (EPA) in response to RCRA place restrictions on the generators of these wastes, including requirements for the manifesting of any wastes to be transported and chain-of-custody liability. These requirements provide, then, some economic incentives for the onsite disposal of the hazardous wastes that are generated on the Nation's 270,000 industrial plant sites (7).

Thermal destruction is a method of disposing of those hazardous wastes which are highly organic. One thermal destruction process is high-temperature incineration, a practice which is regulated by RCRA. Another one is the co-combustion or the co-firing of organic wastes in industrial boilers along with conventional fuels (coal, natural gas, fuel oil). Use of this technique not only destroys the wastes but also allows the recovery of the waste's fuel value which, in turn, lessens the Nation's overall consumption of scarce fuels.

The primary purpose of industrial boilers is the production of energy for onsite process needs. Current RCRA regulations specifically exempt facilities that burn wastes in energy-producing operations from complying with RCRA rules regarding the high-temperature incineration of wastes. These rules require that 99.99 percent destruction and removal efficiency be achieved for the principal organic hazardous constituents (POHC's) contained in the waste to be incinerated.

Industrial boilers offer great potential for the onsite thermal destruction of hazardous waste. If the time and temperature profile of a given boiler is similar to the residence time and exposure temperature required to destroy a given waste, then the disposal of the hazardous waste in the boiler becomes a distinct possibility, one worthy of further evaluation (2). As a first step in this evaluation process, the U.S. EPA awarded a contract to the Acurex Corporation to study the technical worth of the overall concept. This Paper summarizes the findings of Phase I of that study (2).

WASTE/BOILER AVAILABILITY

National figures regarding the amount of hazardous wastes generated in this country are extremely difficult to project. Nonetheless, some attempts have been made. Table 1 presents the results of one such estimate (2,9). The values in this tabulation were based on the assumption that the ratio of the amount of hazardous waste generated by an industry to the number of employees in that industry is approximately constant for each plant in each industry. This is, to say the least, a highly speculative assumption.

Table 1 shows that over 41 million metric tons of hazardous waste are generated each year within 17 of the 19 standard industrial classification (SIC) codes comprising the manufacturing industry plus one non-manufacturing code. Not all of this waste is amenable to thermal destruction however, since some portion of the wastes listed are inorganic. The combustible or organic content of the wastes varies from industry to industry, from perhaps a low of 30 percent in SIC 33 to a high of 80 percent in SIC 24 (2). Consequently, a significant fraction of the 41 million metric tons of hazardous waste generated each year is organic, is combustible, and is amenable to destruction in industrial boilers.

But, are there enough industrial boilers in this country to do the hazardous waste destruction job? There are currently about 367,000 boilers of all types in the United States (8). Of these, about 238,000 can be classified as industrial installations (7,8). Most of these boilers, however, are very small natural gas- or oil-fired firetube units used primarily for space heating. Such "packaged" units do not easily lend themselves to waste co-firing (7). Nonetheless, there remains a substantial number of industrial boilers having capacities larger than 2.9MW (10 million Btu's per hour) which are more suitable for waste co-firing operations. Table 2 reveals that there are about 43,000 industrial boilers in the U.S. over that size (2,3). Table 2 also shows that the boiler population matches fairly well the distribution of waste generators across the U.S., while providing an indication of the regional breakdown of the total amount of organic and inorganic hazardous wastes generated (2).

KINETIC MODEL FOR THE THERMAL DESTRUCTION PROCESS

The EPA/Acurex study set out to develop a mathematical expression that would calculate the amount of residence time needed in an industrial boiler operating over a relatively fixed temperature regime to insure a hazardous waste destruction efficiency of, say, 99.99 percent (or any other required level of detoxification). The physical parameters that influence destruction efficiency are the three T's --- time, temperature and turbulence. The rate of thermal destruction is dependent upon whether the boiler is operating in a true oxidation mode or in a mode approaching pyrolysis in some of the boiler's starved-for-oxygen passages. It is also dependent upon the values of the kinetic constants for the hazardous waste compound (or group of compounds) to be destroyed. If the time, temperature and turbulence requirements to meet the required destruction efficiency of a given compound can be compared to the time, temperature and turbulence conditions that exist in a given boiler, then the ability of the boiler to achieve the desired destruction efficiency can be predicted (2).

TABLE 1. SUMMARY OF ANNUAL HAZARDOUS WASTE GENERATION (1,000 METRIC TONS PER YEAR)(2,9)

SIC Code		Waste Total	Percent of Total
22	Textile mill products	203	0.5
24	Lumber and wood products	87	0.2
25	Furniture and fixtures	36	0.1
26	Paper and allied products	1,296	3.1
27	Printing and publishing	153	0.4
28	Chemicals and allied products	25,510	62.0
29	Petroleum and coal products	2,118	5.1
30	Rubber and miscellaneous plastics products	248	0.6
31	Leather and leather products	474	1.1
32	Stone, clay, and glass products	18	0.1
33	Primary metal industries	4,061	9.8
34	Fabricated metal products	1,997	4.8
35	Machinery, except electrical	323	0.8
36	Electric and electronic equipment	1,092	2.6
37	Transportation equipment	1,241	3.0
38	Instruments and related products	90	0.2
39	Miscellaneous manufacturing industries	319	0.8
40	Non-manufacturing industries	1,971	4.8
	TOTAL	41,237	100.0%

Acurex decided to build into their model a measure of conservatism so that any predictions made would be on the safe side. Consequently, they chose to use a first-order kinetic expression that describes a thermal cracking or pyrolytic decomposition mode because the kinetics of pyrolysis are slower than those of oxidation (2). Slower kinetics translates into conservative estimates of the residence times needed for efficient waste destruction. The rate of disappearance of a hazardous waste constituent by pyrolysis can be expressed by:

$$\frac{dC}{dt} = -kC \qquad (1)$$

where C is the concentration of the constituent at time t and k is the temperature dependent rate constant. Solution of this equation leads to:

$$\ln \frac{C}{C_o} = -Ae^{-E/RT} \Delta t \qquad (2)$$

where C = Concentration of material at residence time Δt
C_o = Concentration of material at time = 0
A = Arrhenius pre-exponential factor, sec^{-1}
E = Energy of activation for bond rupture, cal/g-mole
R = Gas constant, 1.987 cal/g-mole-^oK
T = Temperature, ^oK
Δt = Residence time in the firebox, seconds

Using kinetic data such as that being generated by the University of Dayton Research Institute for the U.S. EPA's Industrial Environmental Research Laboratory in Cincinnati, the A and E values can be obtained for the hazardous waste in

TABLE 2. GEOGRAPHIC DISTRIBUTION OF INDUSTRIAL BOILERS, WASTE GENERATORS AND HAZARDOUS WASTE GENERATED (2,3,9)

	EPA Region										
	I	II	III	IV	V	VI	VII	VIII	IX	X	TOTAL
• Industrial Boilers^{2,3}											
Number of Boilers 2.9-29 MW (10-100 x 10^6 Btu/hr)	2,303	3,080	4,323	9,905	8,283	2,759	3,369	766	2,603	636	38,027
Number of Boilers >29 MW (>100 x 10^6 Btu/hr)	193	302	587	1,053	1,527	671	252	117	183	160	5,045
Total Boilers	2,496	3,382	4,910	10,958	9,810	3,430	3,621	833	2,786	796	43,072
• Waste Generators^{2}											
Number of Waste Generators	3,370	5,260	5,080	6,920	9,800	8,270	2,270	1,570	4,315	1,500	48,355
• Hazardous Waste Generated^{2,9}											
10^3 MT/yr	1,104	3,113	4,354	10,353	6,428	10,533	1,201	318	2,838	995	41,237

question (4). Then, assuming various destruction efficiencies (for example, for 99.99 percent, $C/C_o = 0.0001$), one can make a plot of Residence Time (Δt) versus Destruction Temperature (T). Figure 1 is an example of such a plot; it gives three destruction curves for 2,2',4,5,5' pentachlorobiphenyl, one of the PCB's (2). Figure 1 shows the comparison between thermally decomposing PCB to the 99.99 percent level by either the pyrolysis mode or the air oxidation mode, as well as the pyrolysis mode of destruction to the 99 percent level. Note that pyrolysis is a much slower destruction mode (at the same residence time, a higher temperature is required to get the same destruction efficiency or, conversely, at the same temperature, much more residence time is needed in the pyrolysis mode than in the oxidation mode).

Table 3 presents some A and E values for certain selected hazardous waste constituents (1,2,4,6). With data such as this, use of Equation 2 will yield destruction rate curves similar to Figure 1 for hazardous waste streams of interest.

BOILER TEMPERATURE PROFILE VERSUS RESIDENCE TIME CURVES

To determine what a prospective industrial boiler can do in terms of providing the time and temperature required for efficient waste destruction, one must ascertain what temperatures are reached in its firebox and offgas passages and relate them to bulk gas residence times. A conventional boiler temperature profile, such as the simplified one shown in Figure 2, provides that information (2). Figure 3, on the other hand, is a more complex set of boiler temperature profiles that attempts to illustrate the range of boiler conditions which are often encountered in actual industrial plant operations. Point A' on Figure 3 depicts the exit gas temperature at full-load and mean residence time conditions. Point B' represents the exit gas temperature at full-load and "fast-path" (i.e., one-half of the mean residence time) conditions. Points C' and D' are the respective exit gas temperatures but at half-load conditions. The box connecting these four points has been termed, by Acurex Corporation (2), the "boiler kinetic operational zone", the BKOZ, which of course is the range of outlet conditions typically experienced in normal boiler operations (2). Temperatures above the exit temperature A', for example, are readily found inside the boiler firebox; they are found along the A-A' temperature path, but at lesser residence times.

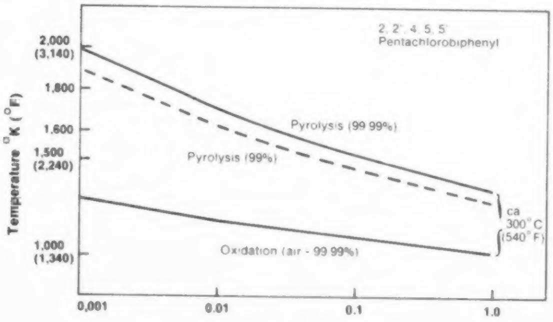

Figure 1 Destruction curves for pentachlorobiphenyl

WASTE DESTRUCTION VERSUS BOILER PROFILE CURVES

To determine if a given hazardous waste can be destroyed in a prospective industrial boiler, one should construct a chart in which the waste destruction rate curves of Figure 1 are superimposed on the boiler temperature profile curves of Figure 3. One such chart is given in Figure 4; on it, the decomposition curves for waste compounds A through E are overlaid onto the temperature profile curves for a given boiler operating under various conditions (2). In this example, Compound E will readily be destroyed because temperatures higher than that required for its destruction are found at every point within the boiler. Conversely, Compound A will not be destroyed because all temperatures found within the boiler are lower than that needed for its destruction. If the boiler were to be operated in only the half-load condition, it is questionable whether Compound B could be destroyed to the efficiency required.

TABLE 3. KINETIC DATA FOR COMPOUNDS OCCURRING IN SELECTED HAZARDOUS WASTE STREAMS (1,2,4,6)

	Oxidation (in air)		Pyrolysis	
	A (sec^{-1})	E (kcal/g-mole)	A (sec^{-1})	E (kcal/g-mole)
Benzene	7.42×10^{21}	95.9	---	---
Hexachlorobenzene	1.9×10^{16}	72.6	---	--
Toluene	2.28×10^{13}	56.5	2.1×10^{12}	77.5
Pentachlorobiphenyl	1.1×10^{16}	70.0	7.44×10^{9}	53.6
Vinyl chloride	3.57×10^{14}	63.3	---	---
Acrylonitrile	2.18×10^{12}	52.1	---	---

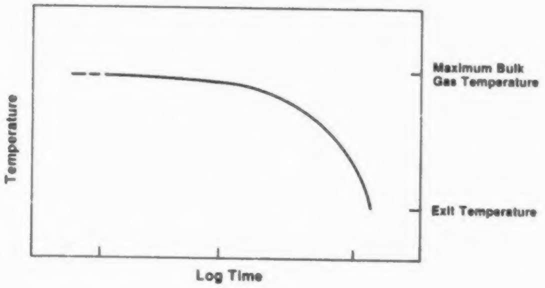

Figure 2 Simplified boiler temperature profile[2]

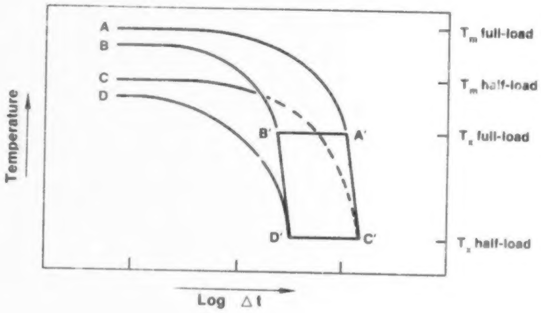

Figure 3 Boiler temperature profiles under full- and half-load conditions (at mean and one-half of mean residence times)[2]

THE KINETIC/BOILER MODEL APPLIED TO TEST BURN DATA: IT WORKS!!

The EPA/Acurex kinetic model described above has been utilized to predict the destruction efficiency to be expected when PCB is co-fired along with conventional fuels in an industrial boiler --- and --- this result was compared with actual test burn data taken by the GCA Corporation for the U.S. EPA during a May, 1980 PCB-burn at the General Motors plant in Bay City, Michigan (2,5).

The GM boiler that was tested was a 17.4 Mw (60 million Btu/hour) watertube unit burning No. 6 distillate oil. The PCB-contaminated waste stream was a waste oil containing approximately 500 ppm Arochlor 1254. The waste stream and distillate oil were mixed in a ratio of 1:10 prior to injection. The boiler was operated at half-load (i.e., the fuel injection rate was half the design rate) (2,5).

The time and temperature profile within the firebox was generated by Acurex using their Zonal Heat Balance Program. Kinetic data were derived from the thermal destruction unit data on 2,2',4, 5,5' pentachlorobiphenyl generated for the U.S. EPA by Duvall at the University of Dayton Research Institute (2,4).

The input data for the kinetic model is summarized in Table 4, and the predictive model diagram is shown in Figure 5. The model predicted that, for half-load and 2.5 percent oxygen content in the firebox, the boiler should achieve greater than 99.99 percent destruction. The actual test results are given in Table 5 and do, in fact, confirm this prediction (2,4,5).

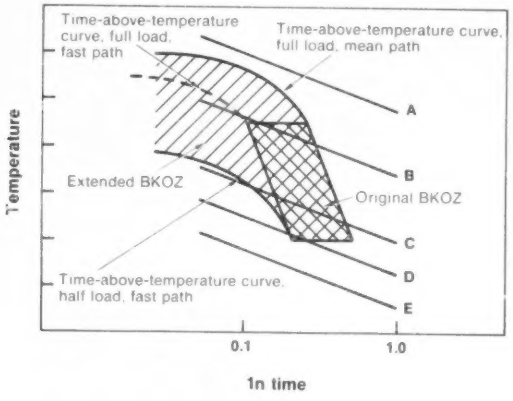

Figure 4. Boiler-compound overlay[2]

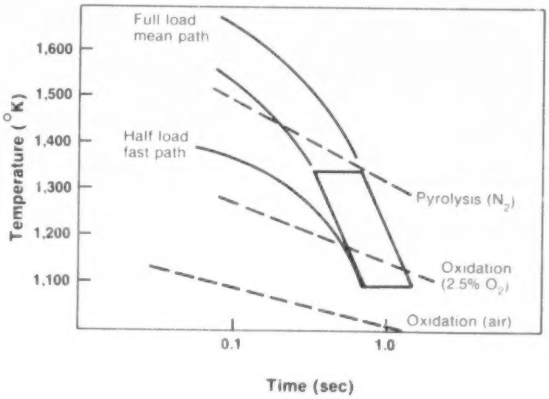

Figure 5. Predictive model diagram for the GM PCB test burn[2]

TABLE 4. INPUT PARAMETERS FOR EXAMPLE CASE MODEL APPLICATION[2,4]

Compound (2,2', 4, 5, 5' - Pentachlorobiphenyl)			
	Pyrolysis	Oxidation (2.5% O_2)	Oxidation (21% O_2)
E (Kcal/g-mole)	53.6	66.7 ± 0.5	70.0
A (sec^{-1})	7.44×10^9	2.6×10^{12}	1.10×10^{16}
Boiler			
T_{max}	1700°K ± 50°	(Flame)	
T_x	1144°K ± 50°	(Back wall)	
t_{mean}	0.4 sec	Acurex boiler zonal heat balance	
t_x	1.8 sec		
(O_2% in flue gas 6^+%)			

TABLE 5. REPORTED DESTRUCTION EFFICIENCY OF PCB'S IN GM's INDUSTRIAL BOILER[2,5]

Run number	PCB in fuel[a] concentration range (mg/kg)	PCB[b] in (mg/min)	PCB out (mg/min)	PCB[c] destruction efficiency (%)
PCB-2	34-72	480-1,000	$< 5.8 \times 10^{-2}$	≥ 99.99[d]
PCB-3	34-76	480-1,100	$< 5.6 \times 10^{-2}$	≥ 99.99[d]
PCB-4	34-76	480-1,100	$< 5.6 \times 10^{-2}$	≥ 99.99[d]

Note: Density of 1:10 Dilution of Waste Oil: No. 6 fuel oil is 3.4 kg/gal.

[a] Based on GM and GCA reported results.

[b] Fuel combustion rate: 3.43 kg/gal x 4 gal/min fuel flow = 14 kg/min.

[c] Percent destruction = $100 \left[\frac{\text{PCB in} - \text{PCB out}}{\text{PCB in}} \right]$

[d] This assumes 100 percent sample collection efficiency. A validated test sample collection efficiency was not conducted as part of this verification burn.

SUMMARY

This Paper can be summarized as follows:

- One estimate shows that about 41 million metric tons of hazardous wastes are generated each year in the U.S.
- Of the 238,000 industrial boilers in this country, about 43,000 of them are larger in capacity than 2.9 Mw (10 million Btu's per hour).
- A first-order kinetic expression has been developed to model the waste destruction efficiency to be expected when hazardous wastes are co-fired along with conventional fuels in industrial boilers. This expression relates destruction efficiency to boiler operating temperature and gas-phase residence time.
- Superimposition of the model-predicted waste destruction curves onto a plot of boiler temperature/residence times allows the prediction of whether a given hazardous waste can be effectively destroyed in a prospective industrial boiler.
- The kinetic model has been utilized to predict PCB destruction efficiency when co-fired with distillate oil in an industrial boiler and the result was compared with actual field data. The model predicted approximately 99.99 percent waste destruction efficiency; this efficiency was corroborated by analysis of the test burn data.

WHERE DO WE GO FROM HERE?

The verification of any kinetic model cannot be achieved when there exists only limited sets of field test data to analyze. To fill the void, the U.S. EPA has embarked upon a Testing Program for Hazardous Waste Co-firing in Industrial Boilers. When the Testing Program starts producing, in mid-1982, additional test data from industrial co-firing operations that are already underway, the current model can be checked for its ability to make accurate, reproducible and verifiable predictions as to what hazardous waste destruction efficiency is possible in a particular kind of boiler.

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BOILER SITE IDENTIFICATION, SAMPLING AND ANALYSIS PROTOCOLS, AND CHARACTERIZATION OF EMISSIONS FROM BOILER TESTS

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C. Dean Wolbach
Robert McCormick
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The development of the Acurex mathematical model predicting the degree of destruction of organic waste in industrial boilers must be followed by actual field testing and further efforts to more quantitatively define the constituents in the exit gas stream. Sponsored by the Incineration Research Branch, IERL, Cincinnati, Ohio, this subsequent field testing program includes several support elements. Using public information, facilities were identified that are cofiring wastes and fuels of interest to EPA; waste and boiler combinations were prioritized; and each operator was approached to request his participation. A sampling and analysis protocol was developed to reflect the data needs of the Office of Environmental Engineering and Technology, the Office of Solid Waste, and the Office of Air Quality Planning and Standards; it includes a pretest engineering assessment, test plan preparation, sampling and analysis procedures, and reporting requirements. Finally, air emissions are being evaluated for principal organic species predicted to be present as products of incomplete destruction of input materials, combustion products, and results of incremental changes to the priority pollutant. This program will establish a data base to support the disposal of wastes in boilers.

SITE IDENTIFICATION

After contacting EPA officials at five regional offices, at all 50 state EPA offices, and in Puerto Rico, we concluded that state air discharge permitting officials and, to a lesser extent, solid waste disposal permitting officials could provide the most information on waste cofiring in boilers. We requested that these officials identify all sites within their jurisdiction where potentially hazardous wastes were being burned in boilers or process heaters, giving as much information as possible on the boilers and wastes burned. Since budget and time limitations precluded a search of permit files, we relied on the personal knowledge of these officials and their colleagues to initially identify such sites, after which limited information on boiler/waste characteristics were obtained from the permit files.

We also conducted a comprehensive search of 20 data bases abstracting government reports and technical literature through the DIALOG Information Retrieval Service offered by Lockheed Information Services. This literature search was extended to the NEDS, SOTDAT, and EADS environmental data systems offered by EPA. We made limited contact with EPA/ORD, EPA/OSW, and EPA/OAQPS personnel, private consultants, and industry representatives as well. Information compiled from RCRA Part B permit applications, required for all hazardous waste disposal, was unavailable at the time of our data search.

Discussion of Results

We identified 129 sites in the United States (not including the pulp and paper industry) where hazardous or potentially hazardous wastes are currently being burned. Since wastes were often identified only as "process residues" or "waste solvents" with occasional specification of the process raw material or product, we could not always determine whether the waste was hazardous under RCRA 3001 guidelines; hence, the qualification "potentially hazardous" waste.

Even less data were available on boiler characteristics. The apparent trend was for primarily liquid wastes to be cofired with fuel oil as the primary fuel, although natural gas and pulverized coal were also listed. We suspect most of the boilers are watertube designs, ranging from small industrial heaters to utility sizes. A significant fraction were apparently designed for waste cofiring; to distinguish between boilers and incinerators with a heat recovery capability, we identified as boilers those units having steam generation as their primary function.

The available data indicate that cofiring of organic chemical process byproducts, spent solvents, and waste oils in boilers is widespread. However, the sites we identified are not a comprehensive listing. Many plants burning wastes, particularly in modified boilers, do not report this to the permitting offices and are even less likely to appear in the literature on waste cofiring. The lack of time and funds to search the EPA permit files and the general limitation of the EPA data bases to boilers having a total uncontrolled criteria pollutant emission potential over 100 tons/yr also preclude a comprehensive listing. But the sites identified were sufficient for representative selection for sampling and analysis.

Site Prioritization and Selection

Our primary objective was to select four to six sites for field testing, covering a range from minimum waste destruction efficiency to maximum performance, which would provide the basis for an across-the-board environmental assessment of hazardous waste cofiring in boilers. Our secondary objective was to select boiler/waste combinations having sufficient operational and kinetic data available to test the Acurex computer model for waste destruction.

Of the organic constituents listed as hazardous on the basis of toxicity under RCRA, light hydrocarbon organic process wastes are the least thermally stable and so represent the best destruction potential. On the other hand, halogenated or complex cyclic or aromatic organics are the most difficult wastes to destroy.

Taking into account the boiler's time-temperatuare profile and how representative it is of the industry, we gave higher priority to standard firetube, suspension-fired watertube, and stoker-fired designs burning coal, fuel oil, or natural gas. Of these boilers, large watertube designs offer superior time-temperature profiles for organic compound destruction while small firetube designs or small stokers represent the worst case for such destruction. We recommend that greater emphasis be placed on the worst case testing.

Table 1 lists the boiler/waste combinations recommended for a six-test matrix. Final site selection requires further investigation since data on boiler design and waste composition for the identified sites were limited. Therefore, we separated the sites into classes based on the available waste characterization data. Class A sites are those burning wastes that can be identified as hazardous. Class B sites are those burning unspecified process residues or waste solvents. Class C sites are those burning waste oils, and class D sites are those burning

TABLE 1. BOILER/WASTE COMBINATIONS FOR A SIX-TEST MATRIX

Boiler type	Waste thermal stability
Large pulverized coal- or residual-oil-fired watertube design	Low
Large residual-oil-fired watertube design	High
Small gas/distillate-oil-fired watertube design	Low
Small gas/distillate-oil-fired watertube design	High
Stoker-fired design, intermediate size range	High
Small gas- or oil-fired firetube design	High

PCB-contaminated oils, as well as all utility-scale boilers.

We recommend that the class A and class B sites be contacted for further information on boiler design/operation and waste composition before final selection is made.

SAMPLING AND ANALYSIS PROTOCOL

The sampling and analysis protocol was developed for use in the test program to generate a data base from which regulations and permit application procedures can be established; characterize multimedia emissions; evaluate the impact of waste cofiring on air pollution control devices; and try and validate the Acurex predictive model for waste destruction. Developed for solid-fuel-fired boilers burning wastes with a high thermal stability, the protocol includes instructions for conducting the field test program, analyzing the collected samples, and preparing the sampling/analysis reports.

Pretest Site Survey

This 1-day survey involves collecting waste and fuel samples, obtaining boiler design and operating data, acquiring meteorological data, and performing a site sampling evaluation.

From the waste and fuel samples, the major organic components present are identified and quantified. To minimize the quantification effort, the investigator should obtain as much information as possible about the process generating the waste and its likely constituents. These samples will also determine the ultimate and proximate analysis of each, gross flue gas compositions, boiler heat release rates, and trace element content of each for verification of the material balance estimate.

Samples should be labeled and logged on a data sheet. The investigator should determine from plant personnel that these samples are representative of wastes to be fired during the field test program.

From the boiler design and operating characteristics, the destruction efficiencies for organic constituents and the formation of products of incomplete combustion are predicted. From meteorological data available at the nearest weather

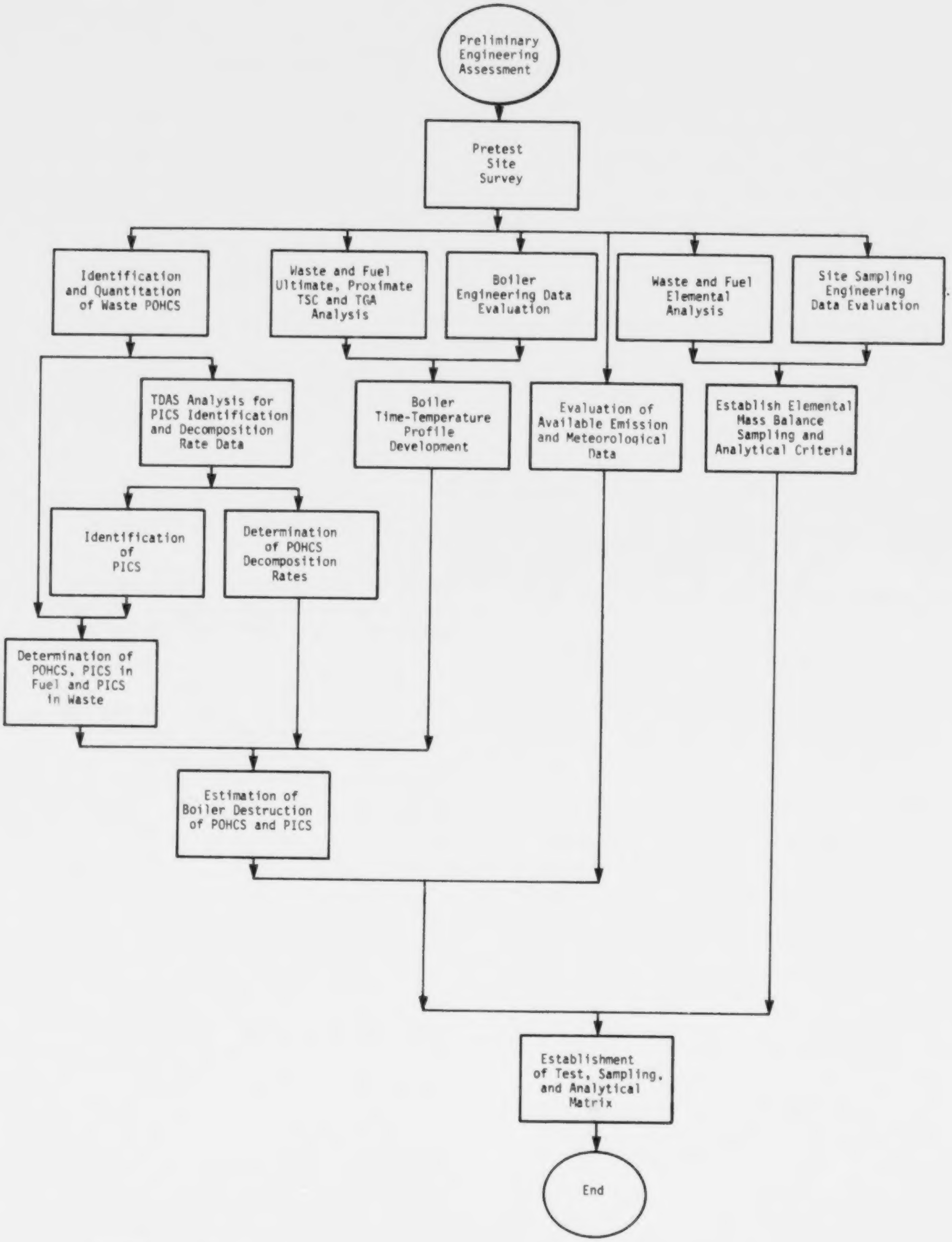
Preliminary Engineering Assessment
Pretest Site Survey
Identification and Quantitation of Waste POHCS
Waste and Fuel Ultimate, Proximate TSC and TGA Analysis
Boiler Engineering Data Evaluation
Waste and Fuel Elemental Analysis
Site Sampling Engineering Data Evaluation
TDAS Analysis for PICS Identification and Decomposition Rate Data
Boiler Time-Temperature Profile Development
Evaluation of Available Emission and Meteorological Data
Establish Elemental Mass Balance Sampling and Analytical Criteria
Identification of PICS
Determination of POHCS Decomposition Rates
Determination of POHCS, PICS in Fuel and PICS in Waste
Estimation of Boiler Destruction of POHCS and PICS
Establishment of Test, Sampling, and Analytical Matrix
End

Figure 1. Preliminary engineering assessment information flow chart.

station, the maximum acceptable stack emissions are calculated as a function of exposure and risk.

The site sampling evaluation covers the plant configuration, components to be sampled, each sampling point, its accessibility, necessary modifications, and other sampling requirements, as well as information on provisions for the test crew's safety, lodging, etc.

All data sheets and samples should be returned to the contractor's office for an analysis that may require up to 4 weeks. Elements involved in this preliminary assessment are outlined in Figure 1.

Waste and Fuel Evaluation

The waste and fuel samples are analyzed to determine and quantify the primary organic constituents present and the waste/fuel combustion characteristics; predict destruction efficiencies and products of incomplete combustion; and supplement the material balance estimates. The analytical protocols and the organic compounds of interest are discussed in the Acurex report prepared under this contract.

Determining the ultimate and proximate analysis of the waste and fuel allows the approximate stack gas composition to be calculated at a given air stoichiometric ratio. The results of thermal gravimetric analysis for volatilization rates and differential scanning calorimetry for heats of vaporization determine the boiler time-temperature profile when cofiring wastes, for input to the predictive model. Finally, a Thermal Decomposition Analytical System (TDAS) determines potential reaction products and their decomposition rates; these data, with the decomposition rates of the organic constituents identified in the samples, are also used in the predictive model. The analytical procedures for obtaining all these data are discussed in the same report.

Boiler Evaluation

By establishing a time-above-temperature profile for the combustion zone, conditions can be determined for destroying a given waste. Time-temperature profiles are computed using an Acurex zonal heat balance computer code. Inputs include the fuel and air properties and boiler operating and design features obtained at the site, and other variables such as turbulence or emissivity based on our experience with combustion processes.

Time-above-temperature profiles, indicating the length of time combustion gases are above a maximum mean temperature, are then generated from the computer outputs. Overlaying a given compound's time and temperature destruction requirements on a boiler's time-above-temperature profile allows various compounds to be screened for destruction efficiencies by noting where the compound line falls under the boiler curve.

Component Destruction Efficiency and Reaction Product Formation

Comparing the possible boiler temperatures from the time-temperature profile with the TDAS output at those temperatures, allows those organic species still present to be identified and quantified and so determine the primary species to look for in the stack gas.

The concentration of these components, which determines the length of each stack test, are calculated using the equation

$$\ln \frac{C}{C_o} = -A \int_{tm}^{t_x} \exp\left[-E/RT(t)\right] dt$$

where

C = Concentration of material at time Δt

C_o = Concentration of material at time o

A = Arrenhuis preexponential factor

t_o = Time at T_{max}

t_x = Mean residence time

E = Reaction energy of activation (cal/g mole)

R = Gas constant (1.987 cal/g mole ^{O}K)

T(t) = Temperature (^{O}K) as function of time in boiler

For compounds of known A and E, the concentration (C) can be calculated. When A and E are unknown, the TDAS data must be further manipulated, using the retention time at a given temperature and the ratio of outlet to inlet concentrations for a variety of test cases to compute A and E.

Given a known input concentration, flue gas volume, and temperature, stack gas concentrations can be estimated.

Establishing the Test Matrix

Using the data assembled in the preliminary assessment, a test plan is formulated by balancing the size of the program against available resources. This test program assumes a large solid-fuel-fired boiler is to be sampled. The formulation process is outlined in Figure 2.

For each operating condition to be tested, including waste-to-fuel ratio, boiler load, or excess air ratio, a baseline test should identify discharges typical of the primary fuel, followed by triplicate tests at the desired waste-to-fuel ratio.

Sampling points should be established to include all fuel and waste input streams, bottom ash discharge, and inlet and outlet streams from the air pollution control device(s). Operating data requirements should be established to include boiler load, waste and fuel temperature, and feed rate, process temperatures, and data to determine fuel combustion efficiency and operational stability.

Sampling methods are dictated by the preliminary assessment. For solid streams (i.e., the solid fuel or bottom ash), grab samples should be taken at hourly or shorter intervals. Liquid samples (i.e., waste) should be collected by grab sampling or automatic compositing samples. Gas phase samples should be collected using an EPA Method 5 or SASS train.

Analytical sensitivities should be reviewed against detection limits. Sample sizes should then be set according to the predicted constituent concentrations and detection limits of the sampling equipment.

Taking a set number of duplicate samples, split samples, spike and recovery sequences, and surrogate samples for each set of test samples ensures meaningful data. Each sample should be labeled and identified on the chain of custody and analysis request forms.

The requirements of the test plan should be compared to the available resources. Funding constraints may require that test parameters be rewritten or low priority options eliminated.

Preparing the Test Plan Document

The test plan document should include the elements listed in Table 2. Acurex computer simulations and predictions will be included as well, along with all pretest data. The EPA technical project monitor and the plant operator must approve the test plan.

Field Testing

Figure 3 outlines the field testing process. A typical test program includes one baseline test, firing the boiler on fuel without waste, and three runs cofiring the boiler on fuel and waste standard settings. One day is required for setup and the Methods 1 through 4 stack gas analyses which involve measuring gas velocity and temperature, determining the presence of

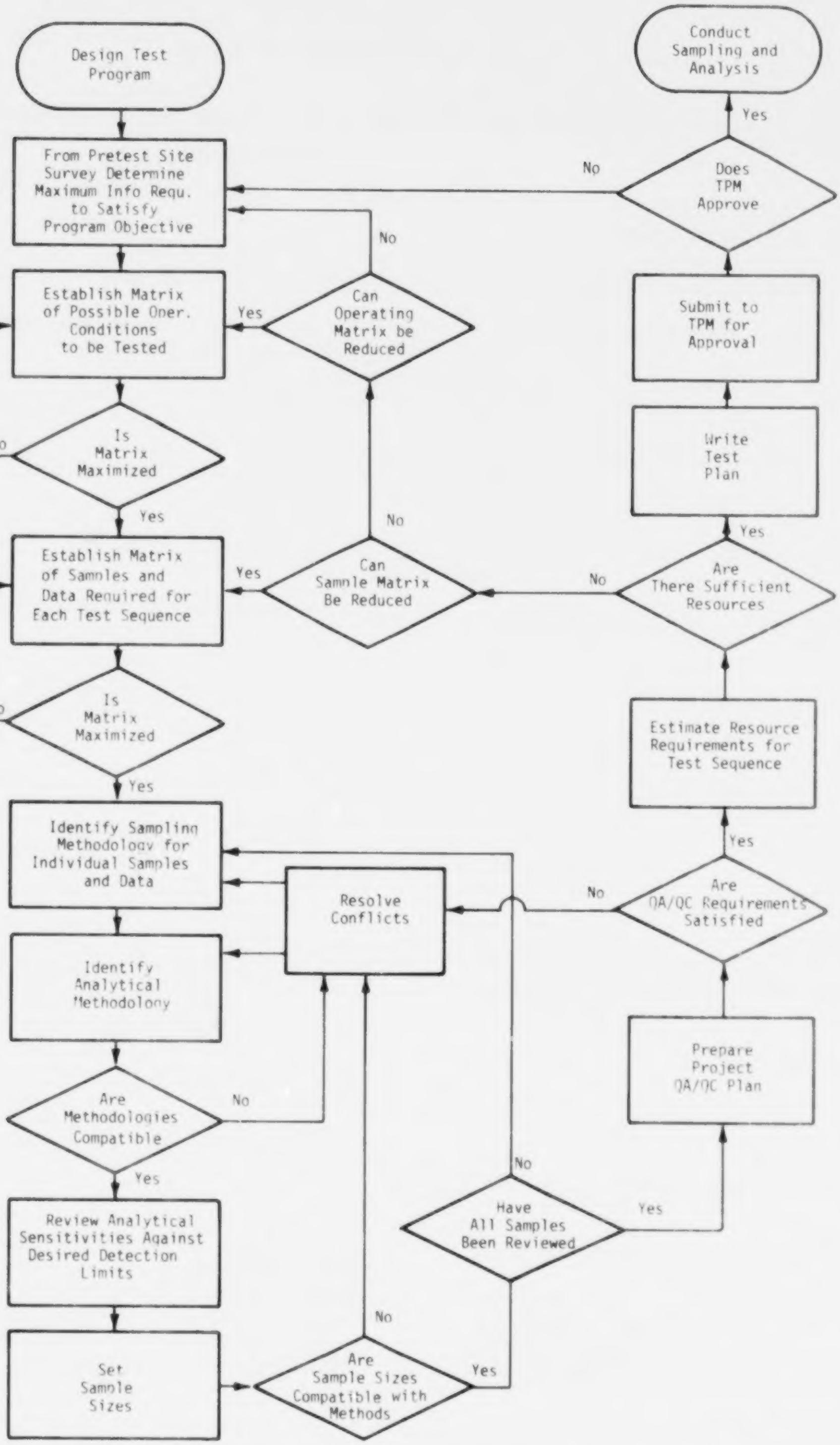
Design Test Program
From Pretest Site Survey Determine Maximum Info Requ. to Satisfy Program Objective
Establish Matrix of Possible Oper. Conditions to be Tested
Is Matrix Maximized
No
Yes
Establish Matrix of Samples and Data Required for Each Test Sequence
Is Matrix Maximized
No
Yes
Identify Sampling Methodology for Individual Samples and Data
Identify Analytical Methodology
Are Methodologies Compatible
No
Yes
Review Analytical Sensitivities Against Desired Detection Limits
Set Sample Sizes
Are Sample Sizes Compatible with Methods
No
Yes
Resolve Conflicts
Can Operating Matrix be Reduced
Yes
No
Can Sample Matrix Be Reduced
Yes
No
Have All Samples Been Reviewed
No
Yes
Conduct Sampling and Analysis
Yes
Does TPM Approve
No
Submit to TPM for Approval
Write Test Plan
Yes
Are There Sufficient Resources
No
Estimate Resource Requirements for Test Sequence
Yes
Are QA/QC Requirements Satisfied
No
Prepare Project QA/QC Plan

Figure 2. Matrix for preparation of testing program.

TABLE 2. TEST PLAN DOCUMENT ORGANIZATION

Section	Description
1. Program Objective	
2. Pretest Site Survey	Agreements with plant contractor commitments
3. Field Test Program	• Test matrix, identifying samples, equipment, test times, personnel, and schedule • Process operating data • Sample storage/transport
4. Analytical Methods	• Sample identification • Description of analyses in generic terms • QA/QC procedures
5. Cost and Schedule	• Site-specific cost impacts, manpower requirements, and schedule

CO_2, O_2, H_2O, and N_2, and calculating molecular weight. Baseline tests are run on the second day and triplicate tests on the following 3 days, including cleanup and teardown. A sixth day is used to finish uncompleted tasks.

The team leader records the data, one person staffs the continuous monitor van, one person takes grab samples, and a team runs the particulate trains. For tests on solid-fuel-fired boilers, as many as seven people may be needed.

Equipment Preparation

Sampling equipment is calibrated and checked before field testing; calibration sheets for gas meters, pilot tubes, and magnahelic gages are completed and filed. Specialized equipment or site modifications should be arranged before arrival at the site.

Field Sampling

Preliminary gas characteristics are determined using Methods 1 through 4 at the beginning of each sampling task and as necessary to account for changes in process conditions.

Source sampling is conducted using continuous monitors to record gaseous emissions and operational variability, and isokinetic sampling to collect organic and particulate materials. The Method 5 particulate sampling train is traversed to sample at several points across the duct. The Source Assessment Sampling System (SASS) which samples at a single point in the duct has three particulate sizing cyclones, an organic module with XAD-2 sorbent, and impinger bottles for trace metal capture. This is used to collect larger sample sizes.

Process data measured to compute boiler efficiency and evaluate cofiring impacts on unit operation will be collected. These operating data will be used to estimate unit efficiency and reduce the emissions sampling data.

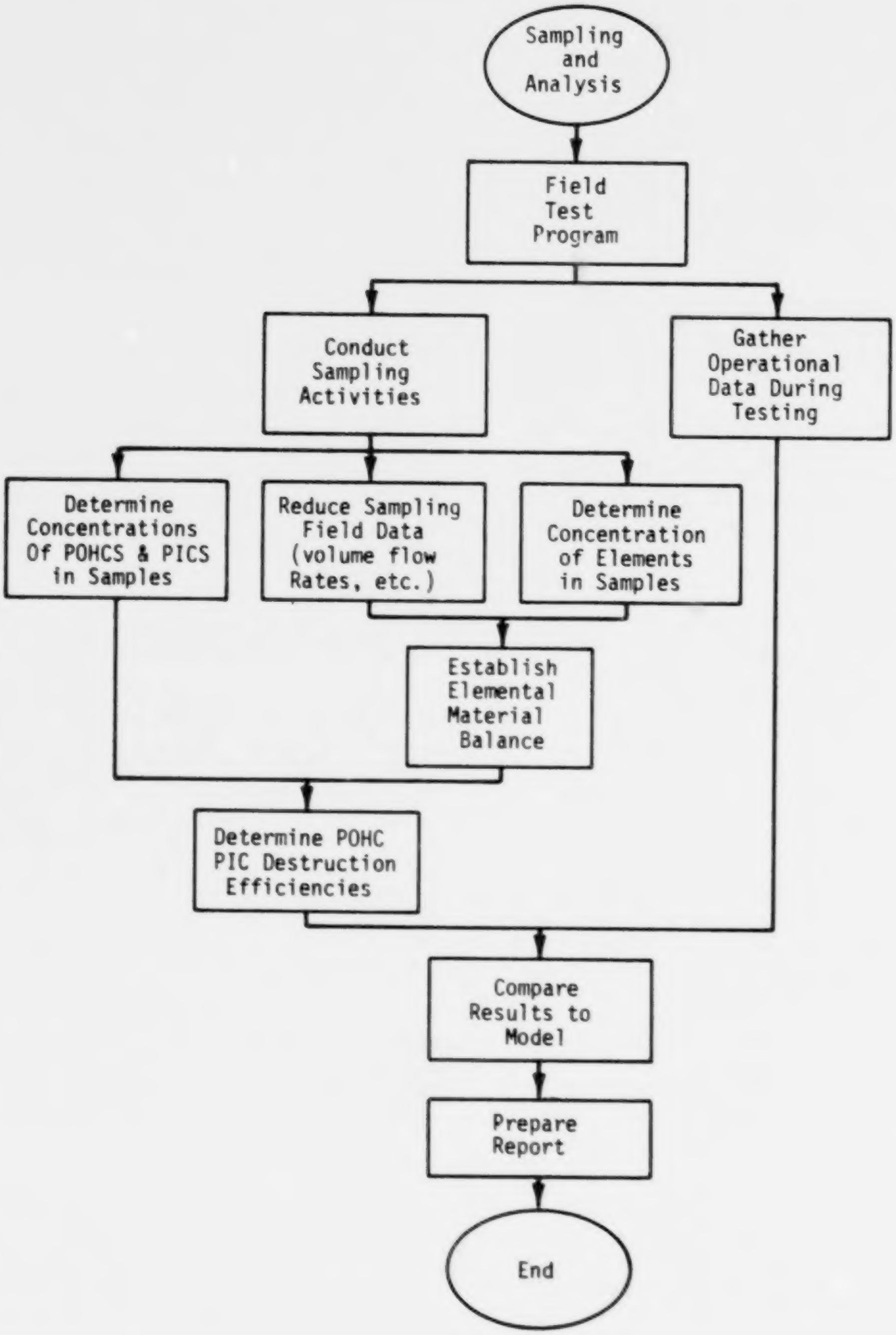
Sampling and Analysis
Field Test Program
Conduct Sampling Activities
Gather Operational Data During Testing
Determine Concentrations Of POHCS & PICS in Samples
Reduce Sampling Field Data (volume flow Rates, etc.)
Determine Concentration of Elements in Samples
Establish Elemental Material Balance
Determine POHC PIC Destruction Efficiencies
Compare Results to Model
Prepare Report
End

Figure 3. Sampling and analysis activities.

Analysis

Posttest analyses of fuel and waste samples, ash grab samples, and the SASS sample catch may include a flue gas analysis of the SASS catch, inorganic analyses for selected trace metals and other species depending on the fuel and waste composition, and organic analyses when it is uncertain which organic species are present. Should these data be already available, these analyses may be eliminated.

Semi- and low-volatility organic compounds are determined with EPA Method 625 involving base/neutral extraction of the sample and extract concentration; the extract is analyzed by combined gas chromatography/mass spectrometry (GC/MS). Each sample is spiked with a surrogate standard prior to extraction, and quantitation is based on comparing specific ion areas in each analysis to that of a standard. Other organic compounds are determined with Method 625 using acid extracts. For both base/neutral and acid extracts, multiple injections of diluted and concentrated extracts are required to quantitate trace and high level species.

Volatile organics are determined using the purge and trap/GC/MS EPA Method 624. Acurex uses a Tekman LSC2 automated purge and trap device interfaced to a Finnegan 4023 GC/MS.

Once the grab sample has been screened and the pollutants for that particular matrix identified, routine methods will be developed to confirm that known methods work for the samples in question. These routine methods are based on the 600 series such as Method 610 for high-pressure liquid chromatographic (HPLC) determinations. All methods are evaluated for precision and accuracy using replicate analyses and spiked samples.

All analyses should be completed within 6 weeks of sample receipt. All samples are saved until the final report has been accepted by the EPA technical project monitor.

Data Reduction

The analytical results will establish the boiler operating parameters and combustion efficiency, destruction efficiency (per component and total), PIC emissions, air pollution control device efficiency, material balance closure, chloride balance, and particulate emissions and size distribution.

The reduced data will be compared to the Acurex model predictions.

EVALUATION OF AIR EMISSIONS

POHC emissions can be estimated by conducting a zonal heat balance, estimating volatilization rates, determining the degree of POHC destruction, and then calculating the emission rate. Products of incomplete combustion pose greater difficulties and are discussed in the following paragraphs.

Products of Incomplete Combustion

The complex mechanisms involved and the lack of information on such mechanisms hamper the prediction of the formation/destruction of products of incomplete combustion (PIC's). Using chemical rate theory, however, upper bounds can be established by reducing a set of pseudo first order kinetic equations to simpler cases that can then be used to develop concentration relationships for PIC formation and destruction.

A set of reaction schemes was developed mathematically with each case representing the disappearance of one component (A) and the formation and disappearance of a product component (P) as follows:

Case I -- All of A converts to P and then P disappears

Case II -- A converts to many different products

Case III -- P is generated from many different components

Case IV -- P is generated by a sequence of reactions in series

Case V -- A converts to P by two different mechanisms

To find $C_P/C_{A,o}$ or the concentration of P at time t with respect to the original concentration of A, we: (1) reduced one or more cases to a simpler, upper bound case; (2) reduced one or more cases to the simple case of the disappearance of P, and; (3) directly compared the concentration of P at time t with that of A at time t, both with respect to A's original concentration.

In case I, $C_P/C_{A,o}$ can be calculated using the empirical pseudo first order disappearance rates for POHC (A) and PIC (P). Calculating the time at which $C_P/C_{A,o}$ is a maximum enables us in many cases to treat the PIC (P) as a POHC. This occurs if the rate of disappearance of P is greater than 100 seconds^{-1}. Most of the other cases can be reduced to case I as an upper bound.

For case II, the concentration of any one P in this system can be intuitively and analytically verified as less than the concentration of P in case I. Therefore, case II reduces to case I as an upper bound.

For case III, the system is mathematically equivalent to a system where a POHC proceeds to a given PIC by several mechanisms. This also reduces to case I as an upper bound by the simple expedient of assuming that all the various waste components proceed to the PIC of interest. This case is not true, but it is a worst case. Case IV represents a much more complicated problem, and a "good" upper bound has not yet been established for the general case. With some stringent limitations, solutions are available. For example, if all the rates are equal, and if all the concentration of the intermediate product are zero at time zero, the following relationships hold (n is the number of steps in the sequence):

$$\frac{C_p}{C_{A,o}} = \frac{(kt)^n}{n!} \exp(-kt),$$

$$t_{max} = \frac{n}{k}, \text{ and}$$

$$\frac{C_{p_{max}}}{C_{a,o}} = \frac{n^n}{n!} \exp(-n)$$

For the situation where all the intermediate rates are faster than the rate of disappearance of the PIC, it can be shown that

$$t_{max} < \frac{n}{k_p}$$

or, in general,

$$t_{max} < \frac{n}{k_{min}}$$

However, the corresponding relationships for concentration are not true. At this time, it can only be said that for $t > n/k_{min}$

$$\frac{C_p}{C_{A,o}} \ll \exp(-k_p t).$$

Case V has not been thoroughly explored. It has been established that

$$t_{max} < \frac{2}{k_{min}}$$

and for the situation where all intermediate rates are greater than k_p and $t > n/k_p$

$$\frac{C_p}{C_{A,o}} < 2\, k_p t \exp(-k_p t).$$

In summary, steps have been taken to set upper bounds on PIC emissions. Some bounds have been set under stringent conditions that do not represent the real world. Our approach to more realistic bounds is currently being pursued and looks promising.

Trace Element Emissions

These elements should partition as in coal or residual-oil-fired boilers, the quantity of any given metal depending on its concentration in the fuel, boiler combustion conditions, the type and efficiency of the air pollution control device (APCD) as a function of particle size, and the properties of the element itself.

Trace metals tend to concentrate in certain waste particle streams of a boiler, leading to the following classifications by stream for partitioning metals:

Class I -- Bottom ash or slag and in the APCD inlet and outlet flyash in approximately the same mass concentrations

Class II -- Flyash, mass entering being less than mass exiting

Class III -- Vapors

Class I elements and oxides are not volatilized in the combustion zone but remain condensed throughout the boiler cycle. Class II elements, however, do volatilize and so concentrate in flyash rather than slag; these elements either form condensation nuclei or condense on existing particulate. Waste burning is not expected to affect trace metal emissions.

Criteria Pollutant Effects

Waste firing will impact the criteria pollutant emissions from a source. The criteria pollutants of concern are particulates, SO_x, NO_x, and CO. In general, it can be expected that emissions will change on a unit-mass-for-unit-mass basis, although this will vary from pollutant to pollutant. If pollutant is generated from element in the fuel, and the element is in concentration C_f in the fuel, then the original pollutant emission rate will be kR_fC_f where k is the fraction of the element converted to the pollutant and R_f is the fuel feed rate in mass per unit time. If the conversion fraction is the same for the fuel and the waste, the new emission rate will be $k(R'_fC_f + R_wC_w)$ where R'_f is the new fuel feed rate, R is the waste feed rate, and C_w is the concentration of element in the waste.

Particulates

Particulate emissions will probably follow this pattern based on ash content. The distribution of ash between bottom ash and flyash may change significantly depending on the nature of the waste ash.

Units not designed to handle ash-containing fuels (e.g., gas- and distillate-oil-fired units) will probably not fire wastes containing ash or mineral-forming elements. Thus, noncarbon particulate emissions are not expected from these units. Carbonaceous materials (soot) may increase or decrease depending on the burnout rate. This is usually controlled under normal boiler operating procedures and is not expected to change under waste firing conditions.

Units designed to handle high-ash content fuels such as the various coal-fired boilers may experience wide fluctuations in particulate emissions. It is expected that, for the most part, the fluctuations will be on the downside. This prediction is based on the fact that most high organic content wastes with high fuel potential will have a lower ash content than the replaced fuel.

Sulfur Oxides Emissions

The generation of sulfur oxides will be directly related to the incremental change in sulfur content of the fuel-waste mixture. Reactivity of flyash to sulfur oxide chemisorption will effect the emissions. The process is straightforward but not simple. Normally, the emissions would be expected to be

$$E_{SO_x} = C_{S,F}R_F + C_{S,W}R_W - A_{S,F}R_{F,A} - A_{S,W}R_{W,A}$$

where

E_{SO_x} = Emission rate of SO_x

$C_{C,F}$ = Molecular weight factor times concentration of sulfur fuel

$C_{S,W}$ = Molecular weight factor times concentration of sulfur waste

R_F = Fuel feed rate

R_W = Waste feed rate

$A_{S,T}$ = Unit chemisorptivity of SO_x on fuel ash

$A_{S,W}$ = Unit chemisorptivity of SO_x on waste ash

$R_{F,A}$ = Rate of ash generation from fuel

$R_{W,A}$ = Rate of ash generation from waste

However, the synergistic effects of the fuel and waste ash chemistries will probably change the unit chemisorbtivity factors in other than a linear manner. Thus, more or less sulfur oxides may be chemisorbed in the ash (on a unit mass basis) than would normally be expected. Waste and fuel ash chemistries also may cause alterations in the sulfur trioxide (SO_3) to sulfur dioxide (SO_2) ratio. Oxidation catalysts such as vanadium and titanium are known to shift the distribution to higher SO_3 content. These types of elements can be expected to be present in many of the waste streams under consideration for boiler destruction.

NO_x Emissions

Nitrogen oxides (NO_x) are formed in combustion processes through two basic mechanisms: The fixation of the nitrogen in the combustion air by oxygen, termed thermal NO_x, and the oxidation of fuel-bound nitrogen termed fuel NO_x. The rate of thermal NO_x formation is highly dependent on local temperatures and, less so, on O_2 concentrations. The detailed mechanisms of fuel NO_x formation are poorly understood, but fuel NO_x formation rates are most affected by local O_2 concentrations, and are relatively independent of temperature.

Since thermal NO_x formation is dependent on temperature and O_2 concentrations, changes in a boiler's combustion conditions attendant with waste cofiring may affect thermal NO_x levels. For example, if excess air levels are increased to facilitate increasing destruction efficiencies, then emitted NO_x levels will increase. Perhaps of greater importance from a thermal NO_x standpoint, though, is if the heat content of the waste cofired is sufficiently different than that of the fuel displaced, then the maximum flame temperature change along with corresponding effects on thermal NO_x prediction. For example, if the heat content per unit mass of the waste cofired is substantially higher than the fuel displaced then flame temperature will increase and thermal NO_x prediction will increase. Corresponding effects leading to lower thermal NO_x formation occur when waste content is substantially less than that of the fuel displaced.

Since fuel NO_x formation derives from oxidation of fuel- (or waste-) bound nitrogen, emitted NO_x levels through this mechanism will be affected depending on the relative nitrogen contents of the waste cofired and the fuel displaced. For example, if a high nitrogen waste is cofired in a distillate-oil-fired boiler (very low nitrogen), emitted NO_x levels due to fuel NO_x will increase. The increase will not reflect total conversion of the added waste nitrogen to NO_x, though. Total conversion of fuel nitrogen to NO_x does not occur for any combustion process. Typical percent fuel nitrogen conversions range from about 20 percent for high nitrogen (1 to 2 percent N) fuels such as some bituminous coals to about 80 percent for very low (less than 0.1 percent N) fuels such as distillate oils (H. B. Mason, et al., Preliminary Environmental Assessment of Combustion Modification Techniques -- Volume II, Technical Results, EPA-600/7-77-119b, October 1977).

In addition, however, other changes in boiler operation attendant with waste cofiring may have significant effects on fuel NO_x production from fuel- and/or waste-bound nitrogen. As was the case for thermal NO_x formation, if excess air levels are raised to help promote waste destruction, then thermal NO_x formation will increase as well. If the burner is retrofit to increase flame distribution and mixing (thereby removing fuel-rich eddies) then fuel NO_x formation will increase.

In summary, NO_x formation by both mechanisms will be increased by positive incremental changes:

- Btu content/unit mass
- Heat release rate
- Excess air
- Flame turbulence

Carbon Monoxide

Carbon monoxide levels should not be affected by combustion of wastes. This is because carbon monoxide concentrations are mechanically controlled to maintain boiler operational efficiency.

EVALUATION OF FEASIBILITY OF INCINERATING HAZARDOUS WASTES IN HIGH-TEMPERATURE INDUSTRIAL PROCESSES

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ABSTRACT

In the search for disposal alternatives, the U.S. Environmental Protection Agency is evaluating the potential use of high-temperature processes for the incineration of hazardous wastes. Many kinds of waste have already been disposed of in boilers and cement kilns; this report considers the many other potential processes, such as metallurgical furnaces, brick and lime kilns, glass furnaces, and sewage sludge combustors. Each process is examined against such criteria as time/temperature profile, geographical location, product quality considerations, institutional factors, and environmental impacts. Promising alternatives are identified.

INTRODUCTION

The Incineration Research Branch of the U.S. Environmental Protection Agency (EPA) has a variety of ongoing programs to investigate, develop, and promote incineration as a means for ultimate destruction of hazardous wastes. One of these programs concerns the use of high-temperature industrial processes. The first processes to be investigated under this program were industrial boilers and cement kilns, which were chosen partially because of their ubiquity and partially because of the interest many boiler and kiln operators expressed in recovering the heating value of wastes. At this point in time several demonstration test burns are either completed or underway.

Interest in other processes prompted EPA to initiate a feasibility screening study for all high-temperature processes. Such a study would provide consistent and uniform criteria for selecting those processes that offer feasible combustion conditions and that should be examined further for overall suitability.

PROCESS SELECTION CRITERIA

The first task was to select common industries using high-temperature processes. Table 1 summarizes the screening criteria against which each process was evaluated.

TABLE 1. SCREENING CRITERIA FOR POTENTIAL HIGH-TEMPERATURE PROCESSES FOR THE DESTRUCTION OF HAZARDOUS WASTE

- Compatibility of process
  - Thermal destruction conditions: temperature and residence time (turbulence not considered)
  - Product quality
  - Potential for fugitive emissions
- Number of facilities
- Geographic matching of industry location and waste generators

The initial list of processes was based on operating temperature; any major process with an operating temperature of greater than 1200°F was included. The initial listing of approximately 100 processes included the metallurgical, chemical, and mineral industries and sludge and waste incinerators. When the other criteria in Table 1 were applied, several of these processes were eliminated from consideration.

Gas residence time within the process at the high-temperature condition was an important consideration; the lower the process temperature, the longer the residence time required for 99.99 percent thermal destruction. Turbulence, the other condition necessary for combustion, was not considered because little information is generally available on this parameter. Residence time and product quality considerations eliminated organic and miscellaneous chemical manufacturing processes from consideration. These processes often attain high temperatures in reactors, but residence times are quite short.

Product quality, both actual and perceived, was an important consideration. Destructing hazardous waste in a steel furnace, for example, could increase trace elements in the steel and affect its physical properties. In all cases hazardous waste disposal was considered secondary to product quality. This criterion eliminated processes such as basic oxygen and electric arc furnaces in the steel industry because these processes produce a high-quality steel that cannot tolerate residues from hazardous waste destruction. This criterion also affected chemical manufacturing, food processing (human and animal consumption), and petroleum refining processes.

The more potential a process had for fugitive emissions, the less likely it is to be suitable for hazardous waste disposal. Raw materials handling procedures affect the potential of a process for fugitive emissions and for hazardous waste disposal. In a sintering process at an iron and steel mill, for example, open conveyors are used to transport raw materials to the pug mill (mixing device) and to the sinter strand, which is also open. Because of the major modifications to the materials-handling system that would be required to correct this high potential for fugitive emissions and because of the short residence time at the maximum temperature of about 2200°F,* the iron and steel sintering process was eliminated from consideration.

The number of facilities available in the hazardous waste generation areas was another major consideration. For example, specialty processes that existed at only a few widely scattered locations or developing processes that were currently operational at only a few sites were not considered. The processes selected for detailed analysis were those that had the potential for disposing of significant quantities of hazardous wastes.

Table 2 lists those industries and processes that remained after several processes had been eliminated from further consideration by the application of the screening criteria. These processes were evaluated in more detail by use of a hazardous waste destruction model derived from an earlier model developed by Acurex Corporation (1).

HAZARDOUS WASTE DESTRUCTION MODEL

The efficient destruction of hazardous wastes in any industrial process is primarily dependent on the temperature and residence time of the combustion products in the furnace employed by the process. Hence, a matching of the residence time-temperature relationship for the industrial process with that required for complete destruction (99.99%) of the hazardous waste should enable one to identify potentially destructible hazardous waste categories. Based on kinetic data for the constituents in the wastes, characteristic curves showing various time-temperature combinations for destruction of the wastes were obtained. For the industrial process, knowing the furnace volume, volumetric flow rate of gases, and temperature range of the furnace made it possible to plot "process curves" that showed the residence time at which the furnace gas is above a certain temperature within the furnace. By laying the "process curves" over the hazardous waste characteristic curves, it was possible to

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* Refer to conversions table at the end of the paper for metric equivalents to English units used throughout.

TABLE 2. INDUSTRIES AND PROCESSES SELECTED FOR FURTHER HAZARDOUS WASTE DESTRUCTION EVALUATION

Industry	Process or furnace	Exit and maximum temperatures (°F)	Residence time (seconds, unless otherwise noted)[*]
Brick	Tunnel kiln	500-2150	4.3
Carbon black	Oil furnace process	1600-2550	1.1
Primary copper	Reverberatory furnace	2370-2570	2.2
Primary lead	Blast furnace	1300-2200	5.9
Iron and steel	Blast furnace	2000[†]-3400	1.1[‡]
	Open hearth furnace	2200-3250	2.0
Lime	Long rotary kiln	1265-3440	8.3
	Short rotary kiln with stone preheater	2115-3340	7.6
Glass	Melting furnace	1140-2700	4.1
Sewage sludge	Fluid-bed furnace	1400-1600	1.4
	Multiple-hearth furnace	900-1800	0.5
Hazardous waste incineration[#]	Rotary kiln	1500-2900	2.0-2 hours[§]
	Liquid injection	1300-3000	0.5-2

[*] Residence time above the greater of the exit temperature or 1400°F.

[†] Represents estimated temperature at the top of the combustion zone in the blast furnace.

[‡] Residence time has been calculated using 33% of the total furnace volume

[#] Included for comparison only.

[§] The residence time for solids and sludges can be adjusted.

predict the waste categories destructible at various temperatures. The required 99.99 percent destruction is predicted for those wastes whose lines are below and to the left of the process curves.

During a preliminary review the following waste categories were eliminated from consideration because of their low destructibility by high-temperature processes or their high explosion potential: inorganic pigments, inorganic chemicals, explosives, iron and steel, and secondary lead. Other wastes listed in the RCRA Background Document (2) were included in the model and grouped according to nonspecific sources (F series) and specific sources (K series). These categories were plotted according to the required temperature and time for 99.99 percent destruction by use of the relationship:

$$\ell n \, \Delta t = \ell n \left(\frac{9.21}{A}\right) + \frac{E}{RT}$$

where

Δt = time required to reach 99.99 percent destruction, s

A = Arrhenius pre-exponent frequency factor (s^{-1})

E = Energy of activation (Btu/lb-mole)

R = Universal gas constant (1.987 Btu/lb-mole - °R)

T = Absolute temperature (°R)

Figure 1 shows the destruction lines for the selected hazardous waste categories.

Process curves were overlayed on the destruction lines to determine the hazardous waste categories that should be considered for destruction. These process curves were calculated for the gas residence time above specific temperatures by use of the following calculation:

$$t = \frac{31800 \, V}{Q \, (T_e - T_m)} \, \ell n \, \frac{T}{T_m}$$

where

t = residence time above a given temperature (T), s

T_e = process exit temperature, °R

T_m = process maximum temperature, °R

V = volume of process temperature zone, ft^3

Q = volumetric flow rate, scfm

This relationship assumes that gas temperature varies linearly with axial distance between the point of maximum temperature (T_m) and the exit temperature. The relationship was plotted for each process for both the mean residence time as calculated by the equation and the "fast path" residence time (0.5 t). Figure 2 shows the process curves for a short rotary lime kiln.

EXAMPLE PROCESS ANALYSIS

The process analysis included model-derived technical time-temperature considerations, geographic matching of industry location and waste generators, environmental factors, and institutional factors. Although all the processes listed in Table 2 will destruct at least some categories of waste, application of all the analysis criteria indicates that lime kilns provide one of the best candidates.

Figure 2 also shows the time-temperature relationship for rotary lime kilns. Figure 3 shows the 1978-79 geographical distribution of lime kilns according to the Department of Interior (2). Theoretically, all the waste categories considered could be destructed in a typical lime kiln, and as the figure shows, the geographic distribution of these kilns is wide.

Most lime kilns are well controlled by high-energy scrubbers, fabric filters, or electrostatic precipitators. Regulations dictate the use of a scrubber for air pollution control of some wastes (e.g., those containing halogenated hydrocarbons). Any increase in particulate loadings from the burning of hazardous wastes should not create a problem, particularly if the plant is now operating well within allowable particulate emission limits.

Environmental problems could result, however, from the potential formation of hazardous products of combustion. The model considers only the destruction of

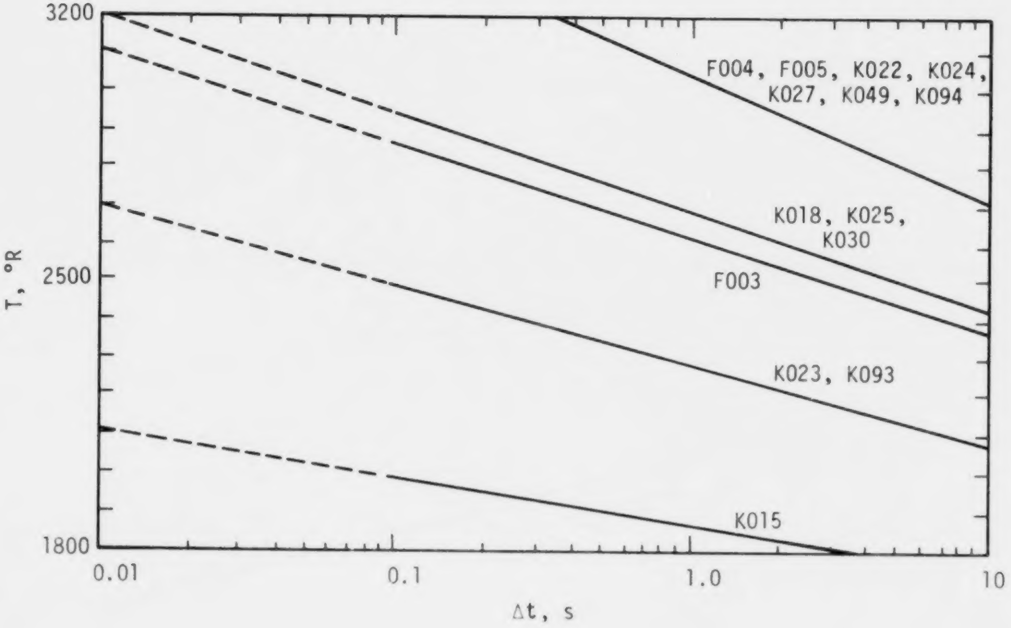

Figure 1. Plots of time-temperature requirements for 99.99 percent destruction of selected hazardous waste categories.

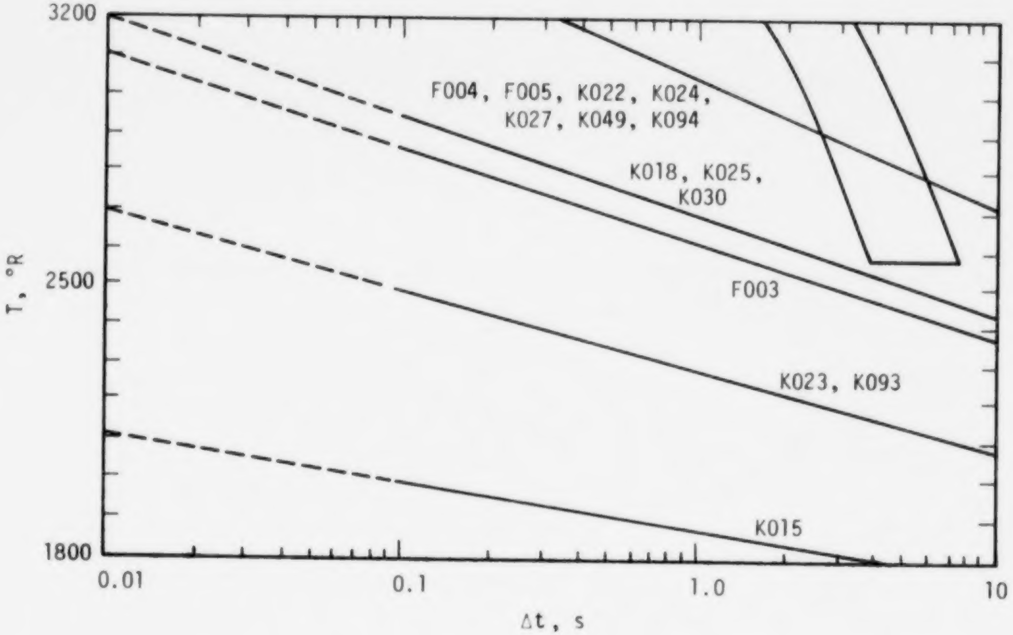

Figure 2. Hazardous waste destructibility for the short rotary lime kiln.

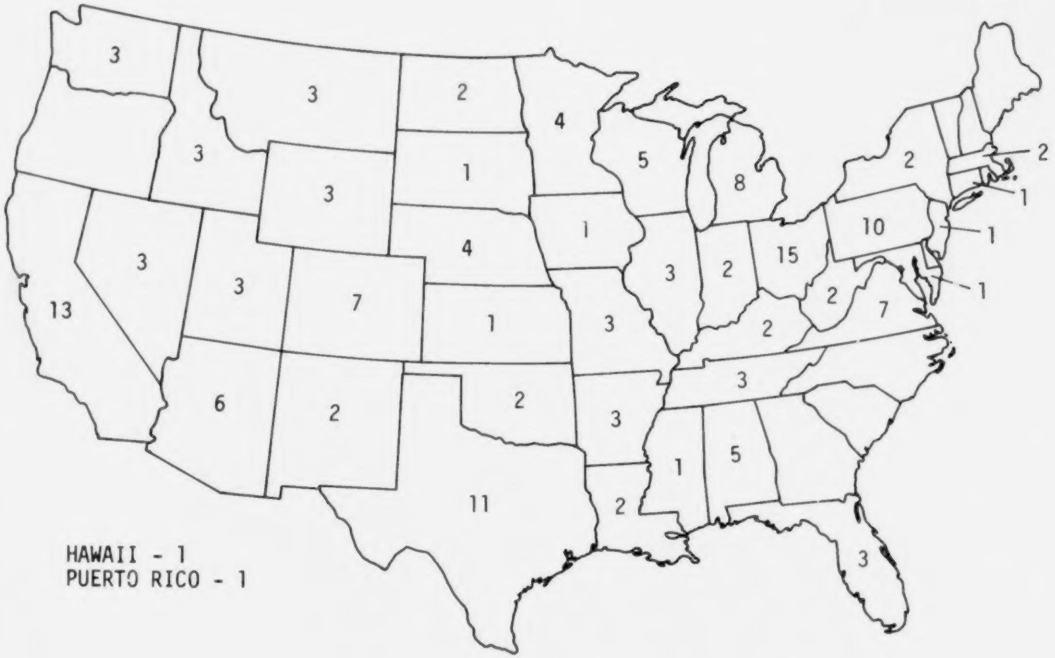

Figure 3. The number of domestic lime plants by state (2).

the waste components and does not predict the compounds generated during combustion.

Institutional factors could be the greatest obstacle to disposing of hazardous wastes in lime kilns. Preliminary contacts with industry representatives have been favorable, however, because of the potential fuel savings from burning combustible wastes.

CONCLUSIONS

The process evaluations and discussions with many persons in industry and government lead to the conclusion that the major impediments to the use of high-temperature processes are both technical factors and institutional factors. The economics of each case have not been evaluated in detail, but will clearly be proportional to the energy cost pressures and the degree of hazard associated with the waste. The term hazardous waste is an unfortunate one because it raises a uniform sceptre of alarm for a universe of materials which vary from deadly toxins to everyday household substances. This raises public concern over utilizing existing high temperature sources, most of which are located in urbanized areas. Similarly, it magnifies worker concern over exposure and potential accidents.

The driving force to utilize high-temperature processes must come from the companies involved. The availability of low- or zero-cost energy combined with possible disposal fees from generators must be sufficiently attractive to justify the effort required to conduct test burns, make the necessary modifications, and convince disparagers of the overall environmental benefit of this approach.

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CONVERSION TABLE

To convert from	To	Multiply by
°F	°C	5.56 (°F-32) E-01
°R	°K	5.56 E-01
ft^3	m^3	2.832 E-02
scfm	Nm^3/s	4.383 E-04
Btu/lb-mole	J/kg-mole	2.324 E+03
Btu/lb-mole °R	J/kg-mole °K	8.314 E+03

A SUGGESTED LABORATORY APPROACH TO SIMPLIFICATION OF THE POHC - PIC DILEMMA*

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INTRODUCTION

Recently promulgated regulations governing the operation of a hazardous waste incinerator (1) are a significant departure from those that govern the thermal disposal of PCBs and PCB-contaminated wastes (2). In the latter case, the PCB disposal regulations carefully specify the range of allowable operating conditions that are required to obtain a permit for the incineration regulations. Regulations issued under the mandate of the Resource Conservation and Recovery Act (RCRA) leave far more to the engineering judgement of the individual permit writer. Specifically, once those hazardous organic compounds in the waste that will most seriously challenge the particular incineration technology, the principal organic hazardous constituents (POHCs) are chosen, it is then required that the necessary operating conditions for the incinerator be identified that will insure the attainment of the destruction and removal efficiency (DRE) that is required for each POHC, i.e., a DRE of at least 99.99 percent.

Obviously, this approach requires a considerable amount of information, both for the would-be permittee, as well as for the permit writer. The question of availability of thermal stability information will be treated below. Here it is important to discuss the problems that are inherent in the requirement that the POHCs be first identified from the large number of compounds that make up a typical industrial waste stream. We are specially concerned with those waste that have been classified and/or listed by the Agency as hazardous. Therefore, one might suspect that the compounds that cause the waste to be classified as hazardous would be the most likely POHCs. An example that illustrates this point is benzene. A waste containing benzene would likely be classified as hazardous due to the fact that it is a suspected carcinogen. However, benzene also contains sufficient heat content, more than 15,000 Btu/lb, thus it has a considerable fuel value. Such a compound, although properly classified as a POHC, would not seriously challenge a properly operating incinerator (i.e., one operating in a fuel lean oxidizing environment).

A waste containing hexachlorobenzene (HCB) may not be classified as hazardous simply based on its known toxicity. However, HCB is known to be one of the most thermally stable organic compounds under most incineration conditions and must be

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*POHC - Principal Organic Hazardous Constituent(s)
PIC - Product(s) of Incomplete Combustion

considered as a POHC for any waste known to contain this particular compound. What is needed is a distinction between those compounds that are toxic by themselves and those compounds that present a challenge to the incinerator so a better POHC classification system can be developed. One way to do this would be through the detailed chemical analysis route. On the basis of the identification of the chemical constituents of a waste, a comparison of the specific thermal characteristics can be made. The identification of the POHCs can then be made. Unfortunately, this body of incinerability data does not presently exist and the process of attaining it could be prohibitively expensive.

In recognition of the fact that there simply was not enough data on the incineration characteristics of even the most common industrial compounds, and the fact that full-scale test burns would be far too expensive and time consuming, the U.S. Environmental Protection Agency (USEPA) sponsored a research program at the University of Dayton Research Institute (UDRI) (3) for the design, fabrication, and operation of a laboratory-scale process to simulate nonflame thermal decomposition environments. What has evolved has become known as the thermal decomposition analytical system (TDAS) (4).

CONCEPT AND BASIC DESIGN OF TDAS

The rationale behind the design concept of the TDAS has not changed basically from that of the earlier discontinuous system (5, 6). The sample is still inserted into the system and then gradually vaporized in a flowing carrier gas. The vaporized compounds are subsequently subjected to a controlled, high-temperature exposure. The components of the vaporized mixture that emerge from the high-temperature environment are then collected and subjected to instrumental chemical analysis. This same thermal analysis format has been employed with respect to the TDAS, but each operation within the system is much more sophisticated, thereby producing greatly increased experimental versatility.

The major design changes over the earlier system are centered around the design of the reactor, the closed continuous system concept, and also the vastly increased analytical capability that is now provided by an in-line gas chromatograph/mass spectrometer/dedicated computer (GCMS-COMP).

Many design objectives were associated with the development of the TDAS. This system should be capable of conducting precise thermal decomposition tests. More precisely, it should be capsble of experimentally determining the effects of the five prominent thermal decomposition variables--exposure temperature, gaseous atmosphere, pressure, mean residence time, and residence time distribution. In addition, the TDAS should be able to accommodate almost any type of organic material. Also, it should be capable of analyzing all of the thermal decomposition effluent products. This closed continuous system should be capable of dealing with toxic materials. Also, the TDAS should be capable of generating data on a quick response basis.

Figure 1 shows a block diagram of the TDAS and Figure 2 is an artist's conception of the assembled TDAS components. Studies can be conducted with the TDAS using almost any compressed gas as the carrier and thermal decomposition atmosphere. Indeed, pyrolytic studies can be performed using inert gases, and oxidative studies can be conducted using air or any other oxygen-containing carrier. Accurate measurements of pressure and flow can be readily obtained with the TDAS. The internal pressure in the reactor and mass flow rate (thus mean residence time) can be continuously monitored by in-stream instrumentation.

In the earlier work with the discontinuous system, only low-volatility organic samples could be tested. The TDAS has been designed for measuring the thermal decomposition properties of a wide range of organic samples--gases, liquids, solids, and even polymers. Complicated organic mixtures can also be tested with the TDAS by using the process of slow vaporization of the sample. After vaporization, the gas phase molecules are subjected to precise high-temperature conditions (these range between 200° and 1150°C and are held with ±2°C) in a fused quartz tube reactor. The emerging products are then rapidly swept into a cryogenic, absorbent in-line trap where the condensable products are captured at temperatures down to minus 110°. The collected effluent products are subsequently thermally desorbed from the trap and then subjected to GC analysis using high-resolution glass, open tubular columns.

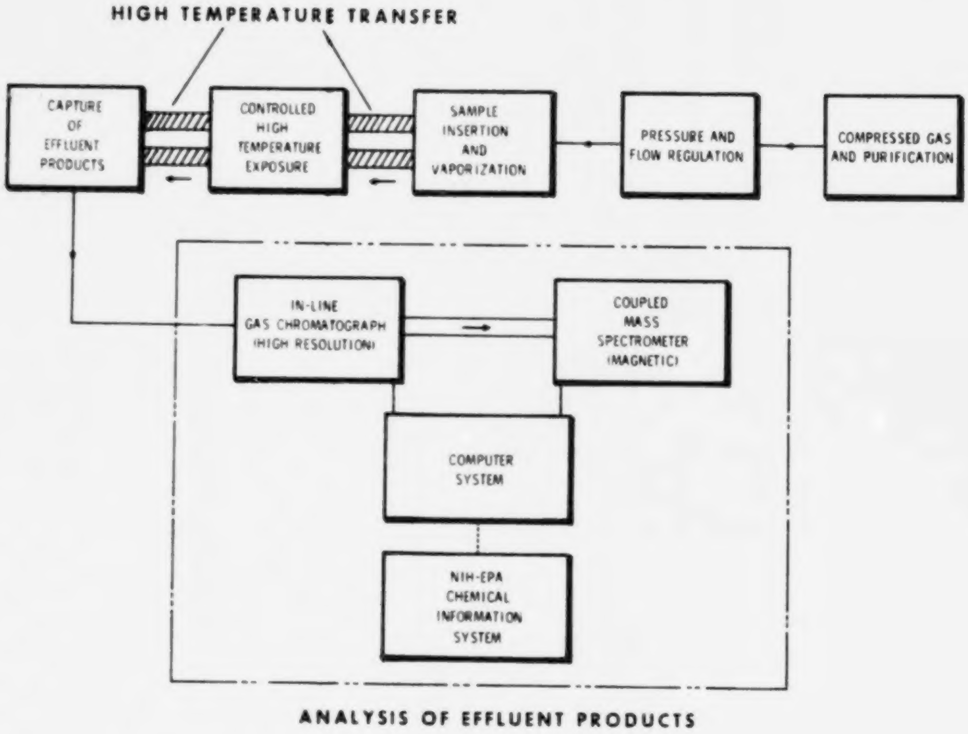
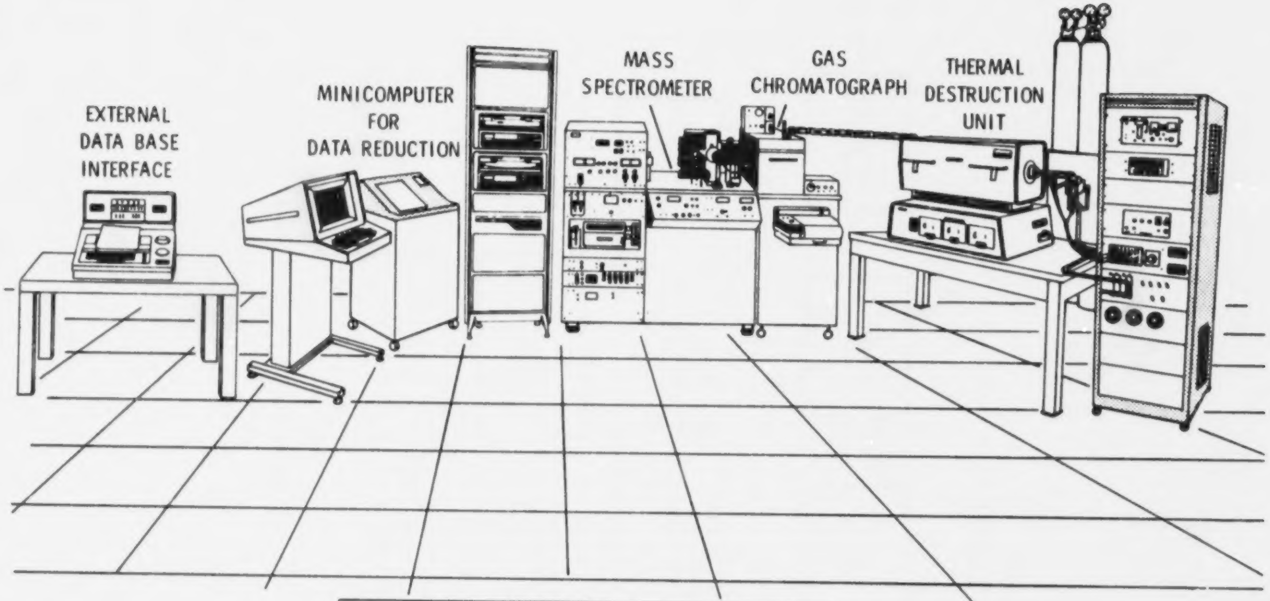

HIGH TEMPERATURE TRANSFER
CAPTURE OF EFFLUENT PRODUCTS
CONTROLLED HIGH TEMPERATURE EXPOSURE
SAMPLE INSERTION AND VAPORIZATION
PRESSURE AND FLOW REGULATION
COMPRESSED GAS AND PURIFICATION
IN-LINE GAS CHROMATOGRAPH (HIGH RESOLUTION)
COUPLED MASS SPECTROMETER (MAGNETIC)
COMPUTER SYSTEM
NIH-EPA CHEMICAL INFORMATION SYSTEM
ANALYSIS OF EFFLUENT PRODUCTS

FIGURE 1



THERMAL DECOMPOSITION ANALYTICAL SYSTEM

FIGURE 2

The separated compounds are then subjected to detailed analysis by mass spectrometry (MS). The thermal decomposition test parameters and the chemical analysis data are then retained, and a complete analysis of the thermal decomposition process is carried out.

Although the TDAS is a complicated system with many interesting components, the operation of this system and the conducting of thermal decomposition tests can be accomplished with relative ease (i.e., after suitable familiarization and experience). Most of the crucial instrumentation for conducting experiments with the TDAS have been mounted in an instrumentation console, and most of the test functions can be continuously monitored on this console.

The basic procedure for testing a particular sample* begins with selection of the thermal decomposition atmosphere or carrier gas. Next the mode of sample insertion must be selected. Then the actual exposure temperature is chosen and each of the furnace zones are set to this temperature. The internal pressure under which the test is to be conducted can be established by adjusting the gas flow restrictors situated downstream of the reactor. The next parameter to be established is the mean residence time. Once the other variables have been stabilized and measured, it is a simple matter of calculating the desired carrier flow and dialing off that value with the adjustable flow control.

After establishing the thermal decomposition test parameters, the next step in the procedure is to cool down the effluent collection trap so that the condensable products can be captured in the absorptive cryogenic trap. The remaining steps are relatively routine. The sample must then be admitted, the products collected, and after switching to helium carrier gas, the captured products must be subjected to in-line analysis by GCMS-COMP.

The above test procedures would yield one set of data points in the thermal decomposition procedure. Any one of the above variables could now be changed for the next thermal decomposition test, and so on, until the thermal decomposition properties of the sample are adequately characterized.

UTILIZATION OF TDAS DERIVED DATA

In support of the vast cleanup at the Morris Foreman Wastewater Treatment Plant in Louisville, Kentucky, UDRI was requested to carry out a TDAS study on "Hex" waste. "Hex" waste being derived from the production of chlorinated pesticides and the waste being established as the cause of contamination of the Louisville sewer system and the cause for shutdown of the treatment plant. The source of the "Hex" was the illegal dumping into the system by waste haulers. Suffice it to say an extremely serious environmental situation existed that required sound remedies to bring the plant back into operation.

Results of the analysis of the basic sample as received are shown in Figure 3. It must be noted here that the analysis indicated that there was at a minimum, 185 compounds present in this waste stream. The principal components of the waste (principal with regard to concentration) are listed in Table 1, with the exception of compound "e" which has been tentatively identified and classed as a major product of incomplete combustion.

A series of controlled TDAS experiments was conducted to determine the thermal stability of the waste and its behavior upon thermal stressing. The results are presented in Figure 4 and show how several major constituents of the waste thermally decompose. Special note should be made of Compound C which was observed to increase in concentration as the waste was exposed to progressively higher temperatures. The compound was identified as hexchlorobenzene (HCB) and it was revealed through the literature that HCB has a high temperature formation process known to the industry. HCB was of concern from several standpoints in this study in that it was a POHC, it was a PIC, and it is one of the most thermally stable compounds investigated on the TDAS.

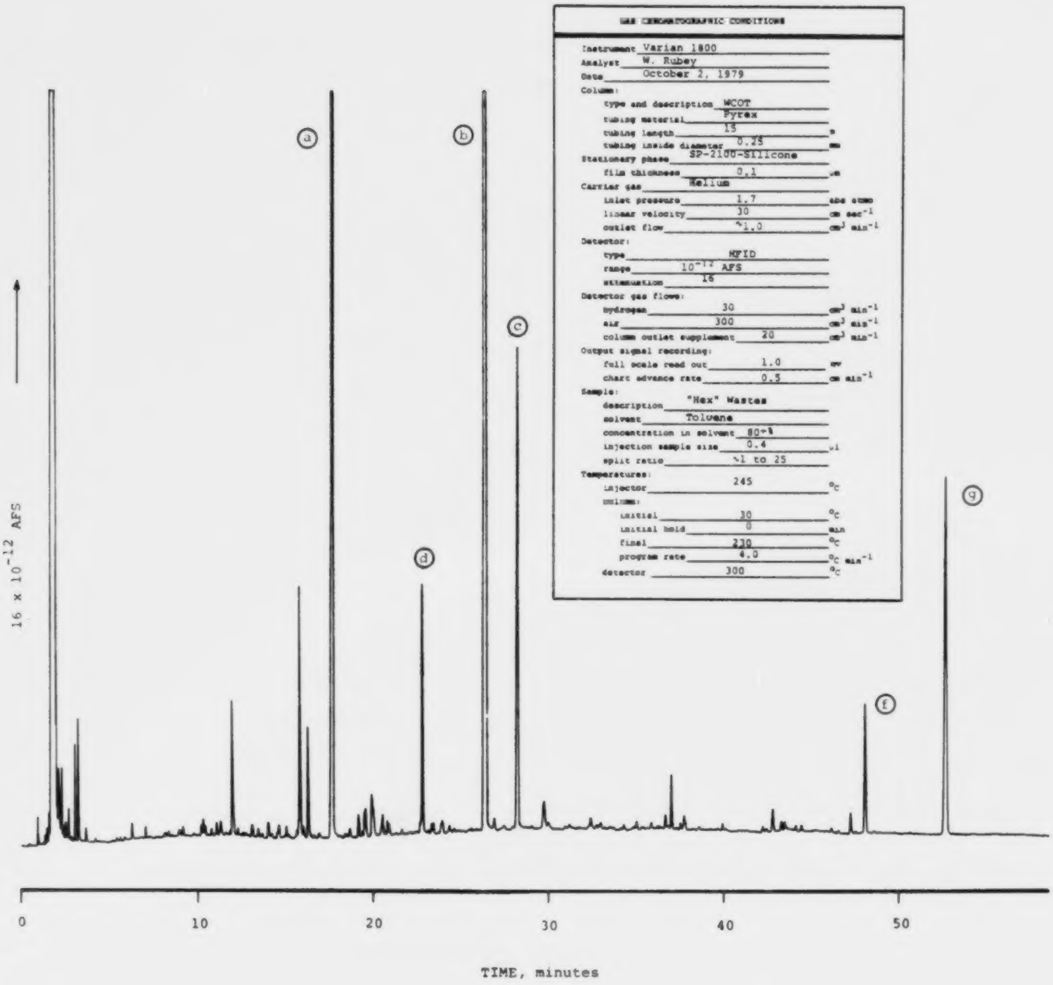
Figure 3 goes on to show that compound "e" was formed during decomposition of the starting material ("Hex" waste) and has the tentative identification of hexchloroindenone assigned to it. Figure 5 is a log-skeletal chromatogram of the "Hex" waste identi-

*All samples subjected to analysis by the TDAS would be screened beforehand using other chromatographic instruments to verify that the sample would indeed be conducive to a TDAS examination.

DESIGNATION	COMPOUND	EMPIRICAL FORMULA
a	HEXACHLOROCYCLOPENTADIENE	C_5Cl_6
b	OCTACHLOROCYCLOPENTENE	C_5Cl_8
c	HEXACHLOROBENZENE	C_6Cl_6
d	PENTACHLOROBENZENE	C_6HCl_5
e	HEXACHLOROINDENONE*	C_9Cl_6O
f	HEPTACHLORONAPHTHALENE	$C_{10}HCl_7$
g	OCTACHLORONAPHTHALENE	$C_{10}Cl_8$

*PROPOSED IDENTIFICATION

TABLE 1 PRINCIPAL WASTE COMPONENTS



GAS CHROMATOGRAPHIC CONDITIONS

Instrument Varian 1800
Analyst W. Rubey
Date October 2, 1979
Column:
  type and description WCOT
  tubing material Pyrex
  tubing length 15 m
  tubing inside diameter 0.25 mm
Stationary phase SP-2100-Silicone
  film thickness 0.1 µm
Carrier gas Helium
  inlet pressure 1.7 abs atmo
  linear velocity 30 cm sec^{-1}
  outlet flow ~1.0 cm^3 min^{-1}
Detector:
  type HFID
  range 10^{-12} AFS
  attenuation 16
Detector gas flows:
  hydrogen 30 cm^3 min^{-1}
  air 300 cm^3 min^{-1}
  column outlet supplement 20 cm^3 min^{-1}
Output signal recording:
  full scale read out 1.0 mv
  chart advance rate 0.5 cm min^{-1}
Sample:
  description "Hex" Wastes
  solvent Toluene
  concentration in solvent 80+%
  injection sample size 0.4 µl
  split ratio ~1 to 25
Temperatures:
  injector 245 °C
  column:
    initial 30 °C
    initial hold 0 min
    final 230 °C
    program rate 4.0 °C min^{-1}
  detector 300 °C

FIGURE 3

THERMAL DECOMPOSITION PROFILES OF 'HEX' WASTE

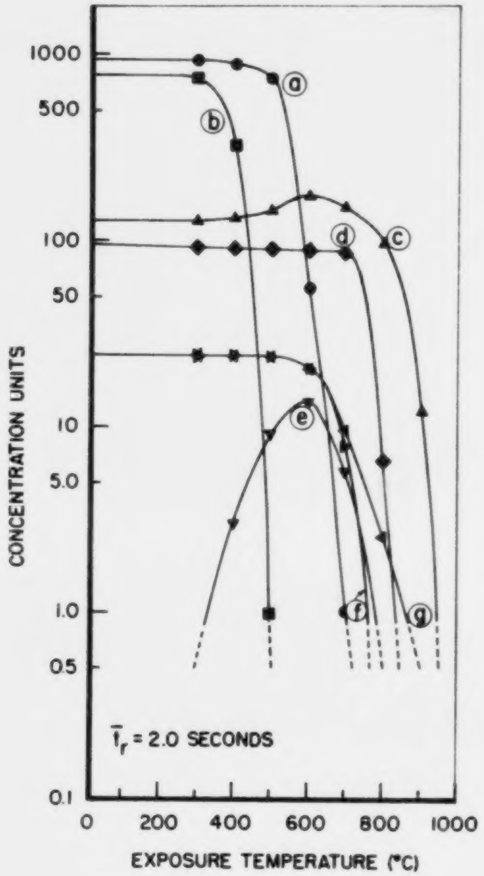


FIGURE 4

fying the six (6) major POHCs. It can be observed from Figure 5, as we proceed from an exposure temperature of 300°C through 1000°C, the change in chromatographic characteristics. There are several PICs that become noticeable during the studies, particularly in the 500° to 700° range.

From the data generated on the TDAS, it was possible to say that the temperature and residence times that were available at the Morris Foreman Plant incinerator would be sufficient for the final disposal of the contaminated sludge. During the actual field disposal of the waste, the incinerator effluent was monitored (7) with the findings that: (a) the contaminated waste was successfully destroyed and (b) the principal chemical species found in the effluent was HCB.

OBSERVATIONS/CONCLUSION

The availability of the TDAS data greatly simplified the work at Louisville by showing that disposal of the contaminated material was feasible and by flagging specific compounds for which the incinerator exhaust gases should be monitored. The overwhelming complexity of the "Hex" waste indicated that chemical analysis of the waste for identification of individual components would be a serious analytical challenge, be very time consuming, and pose severe economic problems. Through the use of the TDAS and exposing a sample to a series of temperatures in a controlled laboratory environment, the entire complexity of the analysis and understanding of the thermal stability of the sample were reduced and clarified.

From the published regulations concerning hazardous waste incineration (1), the definition of a POHC lies in its ability to challenge an incinerator or put another way, its degree of incinerability. At this time, a specific ranking of POHCs via an incinerability index is inconclusive at best. From the results of the "Hex" research on the TDAS and other compounds investigated, it appears that the TDAS may serve as the primary analytical tool in the characterization of a hazardous waste for its POHCs. Again, this was demonstrated in the early log-skeletal chromatograms of the "Hex" waste when on exposure to 300°C, the original waste was reduced to approximately 5.5 percent of its starting compounds. These then become the primary POHCs for this waste and we then proceed with developing the decomposition profiles while being acutely aware of PIC formation during this process. By the discrete interpretation of these results, it becomes possible to identify POHCs in the starting waste for monitoring the incinerators performance and to identify PICs for setting up the analytical requirements for stack gases sampled during the test period.

In conclusion, it is acknowledged that while the TDAS-type of thermal analysis will not take the place of field situation test burns in support of RCRA incineration permits, it can and does provide an invaluable insight into planning and evaluating the results of such a test burn. Additionally, as the data base of TDAS information grows, there is every expectation that EPA and industry can readily predict the conditions for adequate destruction and/or problems associated with the incineration of industrial wastes.

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6. Carnes, R. A., et al., "A Laboratory Approach to Thermal Degradation of Organic Compounds. In: Proceedings of 70th Annual Meeting of the Air Pollu-

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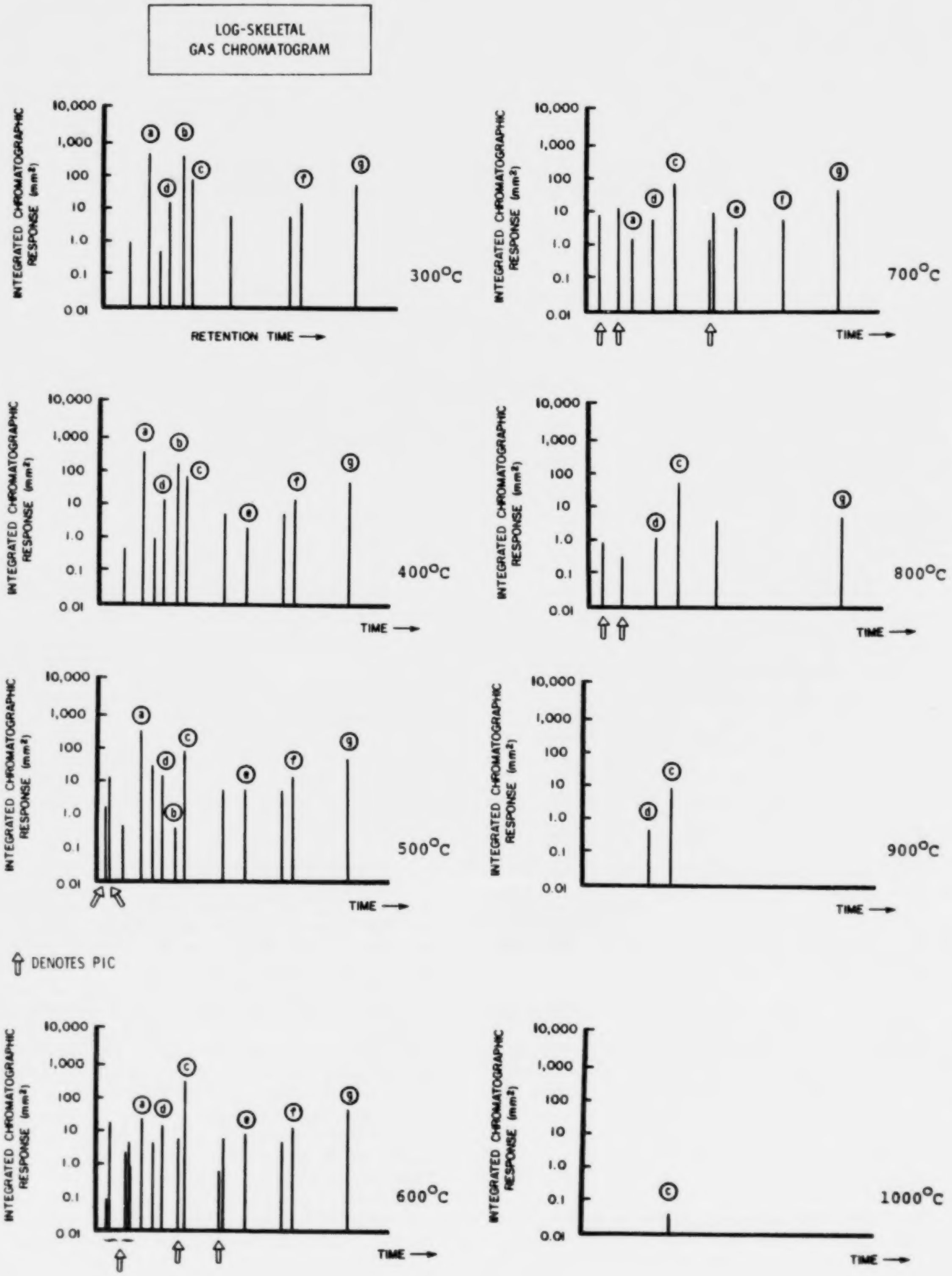
FIGURE 5


LOG-SKELETAL
GAS CHROMATOGRAM
INTEGRATED CHROMATOGRAPHIC RESPONSE (mm²)
10,000
1,000
100
10
1.0
0.1
0.01
RETENTION TIME →
TIME →
a
b
c
d
e
f
g
300°C
400°C
500°C
600°C
700°C
800°C
900°C
1000°C
⇧ DENOTES PIC

SITING AND DESIGN CONSIDERATION FOR THE ENVIRONMENTAL PROTECTION AGENCY COMBUSTION RESEARCH FACILITY

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BACKGROUND

In 1975, the EPA published the results of a major research program entitled "Determination of Incinerator Operating Conditions Necessary for Safe Disposal of Pesticides" (1). This report presented the results of a number of incineration tests covering several pesticide formulations and molecular structures. At that time, it represented the Agency's first attempt to define safe operating conditions for the thermal destruction of hazardous substances. Further, under the authority granted the Agency by the Resource Conservation and Recovery Act of 1976 (RCRA), the Agency used this report along with other documents (2) to support the establishment of incineration conditions that are required for the incineration of hazardous wastes as listed in appropriate Federal Register publications (3, 4).

During the regulatory development exercise, it became apparent that a considerably greater amount of incineration data would be required for the enormous number of compounds and mixtures of compounds to be regulated under RCRA. A major research and development effort was determined to be necessary to provide that data. This program was planned to consist of two major efforts: (a) a laboratory research program to provide basic data on the thermal stability of specific hazardous compounds, which would also support the second effort; (b) an extensive series of full-scale test burns using existing equipment and facilities.

It soon became apparent in other related work that there were significant differences in data observed in the large-scale experiments from those derived from the laboratory studies. Such differences are thought to arise from the simplifications that have been made in the incineration conditions maintained in the laboratory-scale experiments.

A need was recognized for an intermediate-scale study that would more nearly approximate the thermal and chemical conditions that exist in full-scale technology, but at the same time be close enough to the laboratory studies so as to provide a bridge between the two. In July of 1978, a research contract was awarded to conduct parametric investigations of a pilot-scale hazardous waste incinerator. The program was originally scheduled to rent the technology at the manufacturer's facility and have contract personnel conduct the necessary experiments on an intermittent basis so as not to disrupt activities of the manufacturer. Unfortunately, this procedure was found to be unsatisfactory for a number of reasons including the inability of the manufacturer to make the equipment available. Eventually, the EPA authorized the contractor to purchase the incinerator and move it to a suitable site at which the experiments would be carried out.

The contractor found a suitable isolated site that was zoned for industrial research and development and that was within commuting distance from his office and laboratories. Permits were received from the state. All agreements were drawn up and modifications to the site initiated, when local citizens became concerned and effectively blocked the continuation of the program. A very vital lesson in communication was learned and subsequently reported on in the literature (6).

NATIONAL SITE SEARCH

In September 1979, after the two siting failures, the authors were charged by the Agency to find an acceptable site, preferably on Government-owned land, for the incinerator and to conduct the research at that site. An analysis of the earlier siting failures strongly suggested that the public would never accept the concept of this type of research being carried out in anything suggesting a makeshift facility. What was required would be a fully dedicated facility specifically designed for incineration research and for the handling of hazardous materials. As an essential first step in the search for suitable facilities, it was required that the criteria for such a laboratory facility be carefully outlined and a general layout for the facility be designed. The details of the resulting facility will be treated below, suffice it to say here that the essential criteria were defined as follows: (a) the laboratory must be staffed and equipped so as to be capable of on-site analyses of both the incoming candidate waste streams and of all effluent streams from the facility; (b) the operations should be entirely professional and the resulting data made available to the interested public; (c) safety of the operating personnel, the facility, and the surrounding area must be the first consideration in all operations; and (d) since recently published data (7) indicate that the products of incomplete combustion (PICs) may, in many cases be significantly more hazardous than the components of the waste that require the latter to be classified as hazardous, the laboratory must be of a quality to allow the safe handling of toxic materials including carcinogens. With these criteria in hand, an exhaustive site search was undertaken. The approach was, in every case, begun by a search of available Government space (this was selected as a criterion since thereby it would be possible to avoid zoning problems) followed by direct contact with the responsible authorities at the available sites. In most cases, very little enthusiasm was exhibited so that no further action was necessary. Eventually, the National Center for Toxicological Research (NCTR) in Jefferson, Arkansas, suggested that they could and would make space available. The authors visited the decision officials, were well received, and shown that the site was ideal for the proposed facility. Specifically, NCTR is located on the northern boundary of the Pine Bluff Arsenal on a good all-weather road in a location that is sparesely populated and served by a community that is well conditioned to understand the dangers inherent in the handling of explosive and toxic materials (the Arsenal is the national depot of chemical weapons for the Army).

PREPARATION FOR PERMIT OF OPERATIONS

With the approval in principle by the management of NCTR, preparations were begun to obtain the approval of the state and local officials that would be concerned and to properly inform the public of the planned facility (8). Previous experience had shown that the latter element of the informational program was at least as critical as the former. The steps taken were the following:

(1) Confer with and inform the cognizant USEPA Regional Administrator and staff of the proposed facility and its mission.

(2) Confer with and inform the highest state officials of the proposed facility and its planned mission.

When these individuals were satisfied with the general notion and indicated that they would actively support the facility, the next series of steps were taken. Specifically, these consisted of the following:

(3) A series of meetings with the Arkansas Department of Pollution Control and Ecology (DPCE) were held covering the general concept of the facility, its mode of operation, and the nature of the staff were outlined. The meetings finally led to

an application for a construction permit and the assurance that, if there are no public objections, the operating permits would be forthcoming.

(4) A series of meetings with state officials and agencies that would be impacted by the facility. This included the health, police, and transportation departments among others.

(5) A series of meetings with local officials and with the members of the state legislation who represented the area that would be most immediately impacted by the facility.

(6) Civic groups were offered the opportunity for informal (or for that matter, formal) presentations of the planned facility and its mandate.

(7) The state industrial organization were considered important in this informational program since they were concerned with hazardous waste disposal problems, maintained important informational services for the state officials, and could be expected to serve as sources of test materials in the active phase of the research program.

The format of the individual informational meetings was, of course, tailored for the specific group to be addressed. There were, however, many features of each of these meetings that were common. In order to be assured that all parties were aware of the magnitude of the hazardous waste disposal problem in the United States, a slide show using selected examples of the poor practices used in the past and the consequences that all too often have accompanied such practices was presented by Agency officials. After this introduction, the detailed program proposed for the CRF was discussed. In each meeting, sufficient time was allotted for questions from the concerned audience. In some cases, for example with the DPCE of Arkansas, there were a number of meetings, most of which were working sessions wherein the specific requirements for permitting the facility and its operation were discussed and finally incorporated into the construction permit and into the protocol for the operation of the facility.

During this extensive series of infortional meetings and briefings, the media were informed, in detail, by both press conferences and detailed handouts that carefully and fully described the proposed program. Further, the national congressional delegations was kept informed by frequent letters that described the promotional activities that were underway.

The culmination of this activity was a public meeting in Pine Bluff, Arkansas, at which the public was afforded the opportunity to present their questions and possible concerns. The meeting was chaired by the Director of DPCE supported by responsible staff from the Agency and from the EPA Contractor. The attendance at the meeting was approximately equally divided between media persons and the technical and administrative officials there to defend the program. The informational program that had been conducted had apparently answered questions and there was no public concern expressed. Shortly after this meeting, the State of Arkansas issued a contruction permit for the facility.

THE COMBUSTION RESEARCH FACILITY (CRF)

In the course of the discussion between the authors and the officials of the State explicit, as well as, several implicit conditions existed in the permit-conditions that would have a significant impact on the design, staffing, and operation of the CRF.

- Safety assumes such an important aspect in the overall program that a trained specialist (Safety Officer) will be an integral part of the permanent staff.
- The concern about carcinogenic byproducts of combustion required strict adherence to NIOSH and OSHA requirements for the laboratories at CRF.
- Continuous monitoring of all effluents must occur during any incinerator tests.
- The facility must be equipped to conduct the majority of analyses inhouse.
- To the extent possible, all candidate waste streams should originate from within Arkansas.

- To the extent possible, local personnel should be hired to staff the operations.

- The senior staff of the facility must be full-time on site.

When all requirements are brought together, the resulting facility takes the form shown in Figures 1 through 3. The latter figure presents an artist's conception of the interior of the facility. Some of the outstanding features of the facility are:

- The incinerator(s) will be housed in an isolated room accessible only through the change room/shower. All controls and monitoring readout equipment will be monitored from the operations room.

- Each laboratory will be provided with a hood and separate outside air source and will be designed to safely handle carcinogens.

- Internal connections between laboratories have been designed to reduce the potential of cross-contamination to an absolute minimum.

- The characterization laboratory will allow the complete determination of the required combustion conditions for a given waste and to determine the nature of the air pollution control equipment required for each waste.

- The analytical laboratory will be fully equipped to allow analysis of all necessary organic compounds.

FUNCTIONS OF THE CRF

The original purpose of the research program, which eventually lead to the concept of the CRF, was to carry out a number of pilot-scale test burns on materials that had previously been studied at the laboratory scale (9). The purpose of these experiments was to better allow the extrapolation of the laboratory data to large-scale systems and to indicate differences between the idealized laboratory system and the real-world equipment. In the course of the development of that program and spurred by the needs of the EPA, and the requirements stipulated by the State of Arkansas, a number of additional elements of the program to be carried out at the CRF have surfaced. Several of the more important of these will be briefly described below.

WASTE CHARACTERIZATION

It has been stipulated that, prior to the undertaking of a test series on a particular waste, it will be necessary for the staff of the CRF to produce a detailed protocol for the proposed tests. Only after review and acceptance by both the DPCE and the EPA Project Manager, will the actual tests be undertaken. Clearly such a requirement means that the necessary incineration parameters must be established prior to the preparation of such a protocol. It is the function of the Characterization Laboratory (Figure 3) to produce these tests. A literal reading of the Incineration Regulations (4) (1/23/81 - FR) would suggest that this will require the detailed analysis of the wastes for the identification of the principal organic hazardous compounds (POHCs), a determination of which of these POHCs will most seriously challenge the incinerator [and thereby be the compound(s) for which the minimum operating conditions must be determined], and a determination of the air pollution control equipment that is most appropriate.

An alternative procedure to this difficult requirement has been proposed and will be a major element of the program at the CRF. This alternative procedure will, among other results, serve to identify both the POHC(s) for which the incinerator effluents must be sampled and will also serve to suggest the nature of the products of incomplete combustion (PICs) that might be involved.

DEVELOPMENT OF STANDARD PROTOCOLS FOR HIGH TEMPERATURE SAMPLING

The nature of the incinerator technology that will initially be located at the CRF is such that the primary chamber can be operated at sufficiently low temperatures so as to allow the determination of destruction efficiency (DE) as a function of temperature while at the same time operating the secondary chamber at sufficiently high temperatures that assures there are no hazardous effluents. This ability carries the necessity to develop and test various

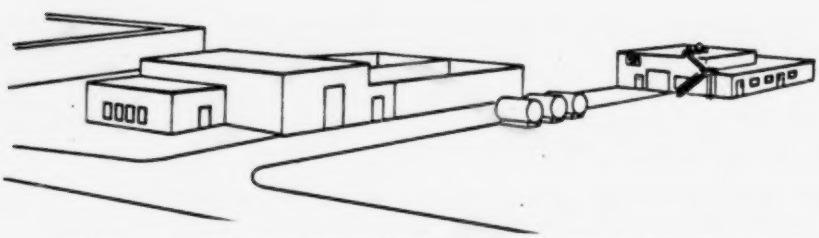

FIGURE 1: RELATIVE POSITION OF PLANNED CRF TO EXISTING POLLUTION CONTROL FACILITIES AT NCTR

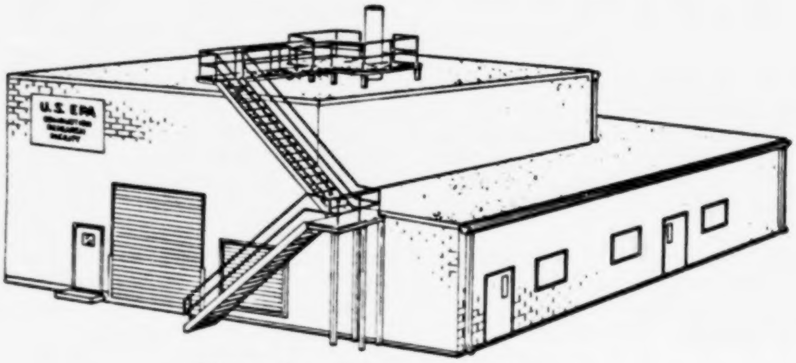

FIGURE 2: CLOSE-UP VIEW OF CRF

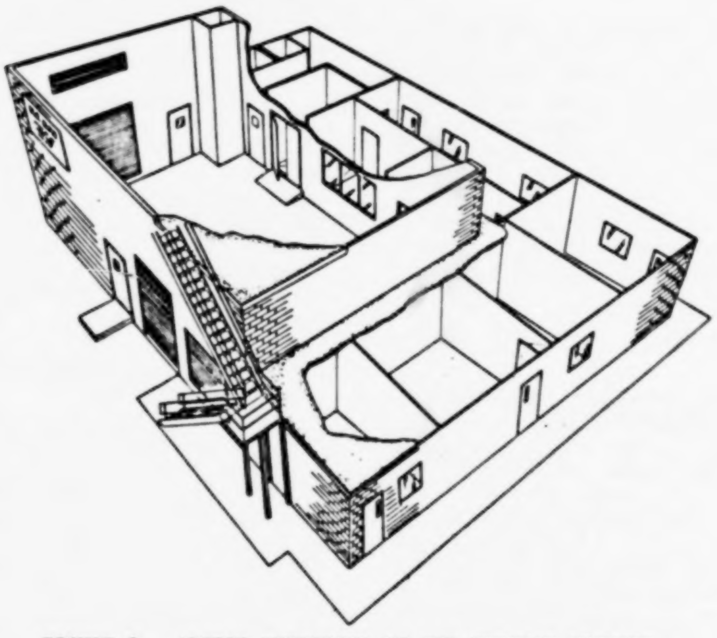

FIGURE 3: ARTIST RENDERING OF CRF CUTAWAY SHOWING LABORATORIES AND INCINERATOR ROOM

hot-zone sampling equipment and procedures. There are a number of practical situations in which a certified and widely accepted sampling method would be of significance.

ANALTYICAL LABORATORY AND PROCEDURES

As has been mentioned, one serious stipulation on the operation of the CRF is the requirement for on-site laboratories to be equipped and staffed so that analyses of any and all effluent streams from the system can be conducted. For many of the anticipated trace compounds there does not exist well established and widely accepted analytical methods. It will be part of the function of this laboratory to assist in the development of such methods where necessary. Furthermore, many of the accepted sampling and collection methods and media have not been adequately verified. This, too, will be part of the mission of this laboratory.

A somewhat esoteric aspect of the research program will be the determination of the effects of sample storage on the validity of analytical data. In most large technology test burns, there is a considerable time lapse between the taking of samples and the subsequent analysis of those samples. There is some concern that during this extended interval relatively short lived species might well be altered either in nature or concentration, or both. A program will be undertaken to determine the possibility of this effect and acceptable methods of control.

INCINERATION INSTRUMENTATION

Presently available original equipment manufacturer (OEM) supplied control instrumentation is not of sufficient range or reliability to adequately meet the control requirements of, for example, the PCB Incineration Regulations (3). It will be necessary that additional instrumentation be developed and tested under standard conditions for the measurement of (on-line and in real time) such parameters as hot zone, mass flow, temperature (both average and temperature fluctuation magnitude), residence time and its fluctuation, and, if possible, the actual concentration of organic compounds in the gaseous effluent from the incinerator. Each of these measurement sensors must be such as to present its output in a form that can be used to control the waste blend feed of an incinerator.

AIR POLLUTION CONTROL DEVICES (APCD)

At present, the major source of operational information on the many different devices that are used for air pollution control is the vendors of that equipment. It would be of great utility if there existed a standard series of tests and test conditions whereby each such device could be treated for its performance and challenged as to its design and capacity. In this manner there would exist data that would then allow the intercomparison of apparently comparable devices under a set of standard conditions. Clearly this would better allow the designer of a facility to make proper judgements. The incinerator at the CRF will be sufficiently well characterized as to allow the design of and the carrying out of such tests.

CONCLUSIONS

One of the disadvantages of the use of trial burns in existing equipment lies in the difficulty in the intercomparison of such data. The present difficulties with the available data base derive principally from this program. It was for the specific purpose of circumventing this inherent uncertainty that the CRF was designed. With the availability of a dedicated facility and a full-time dedicated staff, the rate of return of comparable and reliable data on the thermal characteristics of a variety of industrial waste streams will soon be forthcoming.

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ENVIRONMENTAL AND PERFORMANCE ASSESSMENT AT HAMILTON COUNTY HAZARDOUS WASTE INCINERATOR

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ABSTRACT

This paper offers a brief description of the facility and an overview of the task areas being developed in order to enhance the value of the MSD complex for USEPA and MSD purposes. Another paper to be presented later in this conference describes the results of emissions and combustion efficiency tests conducted in the early fall of 1980.

INTRODUCTION

The MSD serving Cincinnati, Hamilton County and associated municipalities determined a need for a solid and liquid waste incinerator complex to serve the area needs in the late 1960's. Operations were initiated at the facility in 1979.

Recently, Hamilton County and the U.S. Environmental Protection Agency, Incineration Branch, formalized a cooperative agreement whereby the USEPA could begin to participate in the management of the incinerator complex for the purpose of generating data to support permit writing activities for other hazardous waste incinerator complexes. Management of the day-to-day operations of the MSD complex remains with MSD personnel; however, review of past experiences with the facility, possible modifications and improvements to the MSD complex for data generation purposes are presently being planned and will be implemented on a cooperative basis in the near future.

The MSD complex was constructed on the premises of the Millcreek Sewage Treatment Plant, located in the Lower Price Hill area of downtown Cincinnati. The sewage treatment plant includes primary settling and conventional activated sludge treatment facilities. Sludge is treated in sludge digesters to produce methane which fuels a stationary electrical generating plant of 4 mw capacity. Digested sludge is disposed of by multiple hearth incinerators.

DESCRIPTION OF THE SYSTEM

Wastes are most commonly delivered by tanker truck from a variety of sources to the receiving station of the incinerator complex. The waste is pumped from the truck through prestrainers whose round hole openings may be varied from 1/8 in. to 3/8 in. openings according to information available on the waste. Selection of the screen is dependent on the viscosity of the material and the known solids content. (The screens are being replaced by continuous shredders to minimize unloading delays.) The wastes are pumped by one or more of four pumps to a holding tank for placement in selected storage tanks in the tank field.

A small drum unloading and discharge area is available for the management of drummed wastes, although the delivery of drummed wastes is not encouraged by MSD. An elevated unloading dock is provided for the removal of drums from trucks and a drum tilt and discharge mechanism into a sump from which wastes are pumped to a holding tank is provided.

From the unloading point, the wastes may be delivered either to the 6,000 gal holding tanks or directly to selected storage tanks of 25,000 gal capacity. The tank farm includes four 6,000 gal preliminary holding tanks and ten 25,000 gal storage tanks, four 12,000 gal storage tanks and an additional 25,000 gal uninsulated tank for fuel oil storage to service the facility.

The entire tank farm is housed on a concrete apron with a concrete spillwall and trench drain which is valved to prevent spills but will allow the removal of rainwater. Drainage from the tank farm is directed to the inlet of the sewage treatment plant or returned to one or more storage tanks. Each waste storage tank is insulated and was originally designed with internal steam heating coils of the suction type. Due to corrosion problems associated with the heating coils and caking of the waste on the coils, which negated their heating efficiency, the heat exchangers in the waste storage tanks were removed. When necessary, wastes are heated by operating a 40 HP mixer on each tank until suitable temperatures and viscosities are achieved. A differential pressure transducer is mounted on the base of each tank to provide continuous digital weight read-outs at the control panel. Tanks are also monitored with a liquid level gauge located in the control room. In general, the tanks in the tank farm are clustered in groups of two or three and each group is served by two or more pumps which may be operated separately or concurrently to remove or to add wastes to each tank. Under normal operating conditions, two of the ten storage tanks are planned to be used for storage of skimmings from clarifiers and primary settling tanks at the municipal sewage treatment plant.

The total diked containment capacity is approximately 650,000 gal. Total tank farm capacity including holding tanks, storage tanks, fuel oil storage, etc. is approximately 460,000 gal, leaving approximately a one and one-half ft freeboard in the event of a catastrophic spill. A complete foamite fire protection system is installed throughout the tank farm. In addition, each tank is overlaid with nitrogen to reduce the possibility of oxidation, polymerization or spontaneous combustion events while waste is stored, loaded or unloaded.

During incinerator operation, the wastes are removed from the storage tanks and combined in one or more of four batching tanks. Wastes are blended according to chemical compatibility and heat content and, thus, provide a relatively uniform fuel value to the combustion systems. A target of 7,500 Btu's per pound is used for blending schedules. The tanks are flat bottom in design and are not washed between different waste charges. To date, no difficulties have been encountered with reactions between waste residues in the tanks and new wastes.

The blended wastes are removed from the batching tanks and delivered to either of two combustion systems. One is a rotary kiln combustion system with the capability of burning liquid wastes in addition to certain types of granular solid materials. The second is a liquid

TABLE 1

Equipment	Volumetric capacity gal/hr	Maximum heat release MMBtu/ hr	°F Maximum temperature	Minimum residence time/sec
Kiln	1200	65	2400	0.6
Cyclone	1200	77	3100	0.1
Combustion chamber	N/A	N/A	2500	2.0

injection combustion chamber. Both of these primary combustion chambers discharge into a secondary combustion chamber.

Table 1 describes the design capacities of the rotary kiln, the liquid injection combustor and the secondary combustion chamber.

Liquid wastes are delivered by heat traced, insulated pipelines from the batching tanks to externally atomized type nozzles in both the rotary kiln and the liquid injection combustion chamber. Atomization was originally provided at these nozzles with steam; however, high steam demand in other operations of the waste water treatment plant created a need to temporarily use compressed air as the atomizing agent. Air is being supplied by portable rotary air compressors pending installation of new dedicated boilers. In addition, compressed air is used to operate all controls in both the tank farm and combustion facilities.

A solids handling system available at the plant has two distinct capabilities. The first is an in-ground hopper for receiving grit by dump truck delivered by the municipal sewage treatment plant. It consists basically of three receiving chambers of approximately 8 cu yd capacity from which solids are removed by screw conveyor and fed to a bucket elevator. The bucket elevator delivers the solids to a lateral conveyor which delivers the material to the gravity feed chute of the rotary kiln. This system could be used for contaminated combustible solids that are finely divided, e.g., PCB-contaminated soil.

Bulky solids may also be handled by the system. A single truck discharge hopper is provided to receive oversize material which is conveyed by a steel plate conveyor to a 150 HP Eidal shredder. The output from the shredder is carried by belt conveyor to the bucket elevator which lifts the material to the discharge point of the rotary kiln. Neither solids handling system is capable of accepting semi-solid material at the present time. In addition, due to the open handling system, solids contaminated with extremely volatile or powdery materials cannot be accepted because of the danger of excessive fugitive emissions from the system. The design could be modified to accept these materials should a waste generator require this type of service.

The rotary kiln combustion chamber is approximately 20 ft in length and 12 ft outside diameter. Inside diameter and length of the kiln are 10 ft and 20 ft. The injection combustion chamber is approximately 6 ft in diameter and 11 ft in length. The secondary combustion chamber is vertically oriented with hot gases entering the base and leaving the top of the chamber. It is cylindrical, approximately 13 ft 6 in. in diameter by 40 ft in height, and surmounted by an emergency stack bypass for use when power or scrubber water is lost. The three combustion chambers are constructed of carbon steel, ASTM A-283, and lined with refractory and insulating brick. Maximum operating temperatures are 3100° F in the liquid injection chamber, 2400° F in the kiln and 2500°F in the combustion chamber exit. Ash and slag are removed in a quench tank and transported via pipeline to a holding lagoon located near the incinerator.

The hot gas flows from the secondary combustion chamber into a horizontal duct where quench water sprays reduce the temperature of the gas stream to 200° F. Thence, they pass into a vertically oriented variable throat venturi scrubber where recirculated water is added to remove particulate matter. The duct work and venturi scrubber are lined with silicon carbide block, while the shell is constructed of Corten (ASTM A-242). The gas stream turns 90° and enters the base of an acid neutralization scrubber. This absorber is vertically oriented, approximately 15 ft in diameter and 30 ft tall, and is of the sieve tray type. Its function is to neutralize acid gases. The scrubber shell is lined with glass flake polyester to minimize corrosion. The trays are 316 stainless steel. Absorber water is supplied from the principal blowdown tank after pH adjustment with 50% caustic (sodium hydroxide) from two standby 10,000 gal storage tanks. The cooled, neutralized gas flow exits the top of the scrubber, passes through a demister and is conducted vertically down to an induced draft fan powered by a 1500 HP motor. The fan housing is lined with rubber and the fan blades are constructed of Inconel 625. Gases exiting the induced draft blower pass into a 7 ft diameter stack approximately 90 ft in height, incorporating sound suppression baffles and constructed of cylindrical sections of 3/16 in. stainless steel. Three pumps are used to supply water to the quench system and to the venturi scrubber. Two more are used to recirculate flow from the blowdown tank to the neutralization scrubber. An emergency water supply mounted on a vertical tower approximately 120 ft in height is designed to supply quench water to the system should pumping capabilities or power be lost to the system. Quench water is supplied for 5 min of operation which is sufficient to allow shutdown of the system and opening of the emergency cap.

After the complete scrubbing system, gas exits at approximately 180° F; emissions are designed to be a maximum of .03 grains per standard cubic foot at 70° F and 12% CO_2. Emission tests have indicated that acid emissions have been completely neutralized, <2 ppm HCl, but that particulate emissions, while within state limits, are about .08 grains per DSCF. Better quenching and improved demisting should allow achievement of the original design goal.

Process control and operation is carried out in a centrally located building housing the main control panel. The control panel offers complete monitoring of both the tank farm and the combustion facilities. The tanks are monitored for both valve position, i.e., in-flow, outflow, non-operation, liquid level, and weight of tanks. Pump motors are indicated to be in an on-off position and valve openings are displayed. Digital read-outs are provided for waste temperatures in each tank. On the combustion system, temperatures are monitored both by drum type direct reading gauge and continuous recorder as well as digital temperature read-out. Temperature monitoring points are at the exits of the rotary kiln and liquid combustion chamber and at the exit of the secondary combustion chamber. Overall system control is based on the Btu content of the waste to be burned. Waste flow is automatically varied to maintain set point temperatures and negative draft in the combustion chamber (about 1-1/2 in. water), venturi pressure drop (28 - 30 in. water), and pH of recirculated water exiting the absorber (6.5 - 7.0) are controlled.

A broad variety of liquid wastes can be burned in the incinerator system. Reasonable quantities of bulky solids may be burned after shredding and granular wastes can be incinerated. A general category of wastes which are currently excluded from the incinerator is semi-solid material that is too viscous to be handled as a pumpable fluid but too sticky to be handled in a dry solids handling system, such as the bucket elevators and conveyor represent. Should a demand for this type of service be sufficiently great, equipment could be added to the system which would allow its combustion.

FUTURE TASK AREAS

The purpose of the cooperative venture between USEPA and MSD is to allow EPA to develop in a cooperative fashion a full scale test and evaluation facility for evaluating the destructive efficacy of the facility on various types of hazardous wastes. The evaluation will include: technical modifications required to increase the facility's production or decrease costs; monitoring requirements to more completely measure emissions; and steps necessary to increase the variety of hazardous wastes which can be and are burned at the facility. Throughout all operations, data will be collected and analyzed to support the permitting of other full scale incineration facilities throughout the United States. Thus, where questions of compatibility of an incinerator with a specific hazardous material cannot be resolved by other data or by the literature, it will be possible for EPA to conduct a preliminary full scale, controlled trial burn on the material in question.

A number of tasks are envisioned to contribute to the modification of facility operations in order to accommodate the EPA requirements for a full scale hazardous waste incinerator test facility. Among those tasks presently being developed are the following:

1. Substantial additional effort will be dedicated to the detailed monitoring of on-going incineration operations at the facility. Included will be a definition and description of all problem areas that are encountered by the facility in order that this information may be passed along to incinerator design personnel. Many areas will be examined as unit operations. This will include personnel assignments, overall management, laboratory operations for monitoring and control of wastes, receiving area operations, storage operations and compatibility control requirements, staging of wastes for combustion, incinerator control operations, and the emission control requirements. In short, a detailed description of operations at the facility will be created to be used as a reference manual for future hazardous waste incinerator operations.

2. A detailed review and documentation of the original plant design vs. the actual plant as it exists will be made. Included in the document will be definitions and reasons for the changes that have been brought about and a description of the types of problems which were overcome by the changes.

3. A quarterly operating cost summary for the facility will be generated in order to indicate the level of cost of operation. Sufficient detail will be developed in the costs in order to show those costs that are accrued while the facility is not in operation, as well as those that are accrued during operation. Modification of the facility costs will also be defined.

4. One area of substantial interest to

both EPA and MSD is the creation of a system which will allow the collection of extensive data on various hazardous waste incineration tests at the lowest possible cost. As a result, a number of alternative approaches to long term sampling and analysis problems of hazardous waste incinerator facilities will be examined. Principal among these will be the preliminary considerations for creating sampling slipstreams from various points in the facility coupled with automatic monitoring instrumentation in an instrument bank and computerized collection and reduction and presentation of the data as it is generated. Such an advanced system would, of course, allow for the accumulation of large quantities of data at very low cost after the initial installation costs of the system.

5. Substantial effort will be dedicated to the classification of the principal organic hazardous constituent groups (POHC's) that have been burned at the facility since its doors opened several years ago. This data collection effort will create a backlog of information concerning those hazardous materials that have been successfully burned at this type of facility.

6. Pursuant to the information developed in (5), a definition of POHC's that may be burned at the facility will also be created. Along with these POHC's, appropriate sources of typical wastes will be compiled. Constraints on the incinerator facility for accepting and burning these materials will be defined. This would include permitting requirements, time required for permits, and the possible quantities and locations of waste that could be accumulated for combustion at the facility.

7. In order to carry out experiments during the period of transition from present operations at the facility to those that might be exemplified by improved data collection systems in the future, an experimental data collection and operating protocol for the facility will be prepared in order that data may be collected on POHC's as soon as possible that may be of immediate interest to EPA permit writers. This protocol would include a detailed definition of operations by the various personnel at the facility, as well as data which should be collected and how it should be collected.

The preceding tasks summarize a number of areas of significant interest to EPA and MSD. A number of other tasks are also being considered for inclusion in the overall scope of the project, either in this initial phase or in future phases. Areas that may be of interest to others in the hazardous waste incineration field would be welcomed as possible suggested tasks for inclusion in the cooperative agreement. These should be submitted to Mr. John Trapp of MSD of Greater Cincinnati or Mr. Donald Oberacker of the USEPA as soon as possible.

At the conclusion of the project, EPA expects to have a full scale test facility representing the most cost effective approach to the gathering of data under carefully controlled and monitored conditions for a variety of POHC's of interest to the Agency. This will be done without altering or interfering with the normal operation of the facility which will continue to earn its own capital repayment and operating expenses through the services rendered.

TRIAL BURN VERIFICATION PROGRAM
FOR HAZARDOUS WASTE INCINERATION

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ABSTRACT

The trial burn protocol described in the EPA Guidance Manual for Evaluating Permit Applications for the Operation of Incinerator Units has been followed in a case study of the Cincinnati Metropolitan Sewer District's (MSD) incineration facility. This paper summarizes trial burn protocol requirements and presents the results of the protocol verification tests carried out at the MSD incineration research facility.

INTRODUCTION

Hazardous waste incineration regulations, as published in the Federal Register, January 23, 1981, include stipulations that will require "trial burns" in incinerators. Therefore, EPA has prepared a Draft Guidance Manual that presents a draft protocol for conducting the trial burns (1). Midwest Research Institute (MRI) has a contract with EPA through Rockwell International to verify the protocol described in the guidance manual, on a case study basis, at the Cincinnati MSD incineration facility. This paper describes the protocol requirements, the incineration facility, and the sampling and analysis that have been carried out to verify the protocol and to determine the performance of the incinerator.

SUMMARY OF TRIAL BURN PROTOCOL REQUIREMENTS

This section summarizes the salient aspects of the trial burn requirements as we understand and interpret them. A more detailed description of the trial burn, including waste analysis and evaluation of incinerator performance, can be found in Reference (1).

The purpose of a trial burn is to (a) demonstrate incinerator operating conditions such that a "new" waste can be burned within the regulatory performance standards and (b) demonstrate that a new incinerator can operate similarly. "New" wastes are defined as those hazardous wastes with compositions different from hazardous wastes specified in the facility permit. Either a trial burn plan must be submitted with each request to incinerate a new waste, or data showing that the waste has been previously incinerated in a similar incinerator in an environmentally safe manner must be submitted. If a trial burn is required by the permitting agency, the following elements must be contained in the trial burn plan.

Waste Analysis

The analysis parameters in this category are heating value, viscosity, concentrations of all hazardous constituents present in the waste, PCB concentrations above 50 ppm, chlorine content, hazardous metals content, kinematic viscosity (for liquids), percent solids (insolubles), ash content, flash point, elemental analysis, water content, and thermogravimetric analysis. The rationale for selection of these parameters and the waste sampling and analysis methods are designated in Reference (1). One of the major objectives of the waste analysis is to select principal organic hazardous constituents (POHCs) for establishing the effectiveness of the incinerator based on the destruction and removal efficiency (DRE) of the selected POHCs. The selection of POHCs is dependent upon the concentration of the POHC in the waste and its heat of combustion, as presented by EPA.

If the hazardous wastes are blended prior to incineration, all the above analyses should be performed on the blend. Also, if an operator wishes to vary the chlorine content, the waste analysis should be reported for each of the various chlorine-containing wastes. If the auxiliary fuel is not a conventional fuel, then the feed to the incinerator should be considered a blended waste.

Descriptions of Incinerator Components

This category includes type of incinerator, manufacturer's name and model number of major components, dimensions of major incinerator components including combustion chamber, description of auxiliary fuel system, nozzle and burner design, capacities of prime movers and manufacturer's curves, stack gas monitoring and pollution control monitoring systems, locations and descriptions for temperature, pressure and flow sensors, and construction materials.

Provisions for Sampling/Analysis and Monitoring of Incineration Process

Procedures and locations for monitoring combustion temperature, waste and fuel feed rates, air flow rates, CO in stack gas, and excess air in stack gas should be described. In addition, equipment and procedures must be specified for determining POHCs in the waste, including sampling and analysis of ash, scrubber effluent, particulate emissions, stack gas flow rate and temperature, POHC concentrations in the waste and stack gas, and HCl concentration in the stack gas.

Trial Burn Operating Conditions and Schedule

Factors included here are combustion zone temperature, waste feed rate, air feed rate, auxiliary fuel feed rate, operating conditions for pollution control devices, and procedures for stopping feed and safely shutting down the incinerator and controlling emissions in case of an emergency. Aspects connected with the schedule are dates of trial burn, duration of trial burn, and quantity of waste to be burned.

CINCINNATI MSD INCINERATION FACILITY

Only a brief summary of the incineration facility is provided in this paper, since there will be another paper completely dedicated to discussing the incineration facility, its various components, and their design features.

The incineration facility at Cincinnati is owned and operated by the City of Cincinnati's MSD. It is a full-scale, modern installation with a liquid injection cyclone furnace and a rotary kiln capable of handling both liquid and solid waste. The system can handle about 151,413 ℓ/day (40,000 gal/day) of waste; the cyclone furnace handles waste at the rate of 75.7 ℓpm (20 gpm) and the kiln about 37.8 ℓpm (10 gpm). The Btu ratings on the cyclone furnace and the kiln are 65×10^6 kJ/h (62×10^6 Btu/h) and 55×10^6 kJ/h (52×10^6 Btu/h), respectively.

The cyclone furnace and the kiln are connected to a common secondary combustion chamber (combustor) which has a volume of 162 m^3 (5,726 ft^3). Combustion gases leaving the combustor are quenched before they enter a venturi scrubber which has an operating pressure drop of 76.2 cm (30 in.) water. From the scrubber, the gases go to a caustic absorber and then exit through the stack. The ash from the combustor and the rotary kiln drop into a four-compartment ash tank which is sluiced to a lagoon once every 8-h shift.

SAMPLING AND ANALYSIS

In keeping with the requirements of a trial burn, the overall objective of the sampling and analysis program was to characterize the waste burned, select the POHCs, determine DREs for the selected POHCs for various incinerator operating conditions, establish particulate grain loadings, and determine chloride removal efficiencies. Present RCRA regulations require 99.99% efficiency for POHC destruction and removal, 99% hydrogen chloride removal efficiency, and a particulate grain loading of 0.183 g/dscm (0.08 gr/dscf) corrected to 12% CO_2.

A schematic illustration of the Cincinnati MSD incineration facility showing the various sampling points is presented in Figure 1. As shown in the figure, liquid waste which was fired in the cyclone furnace as well as the rotary kiln was sampled. In addition, one sample of the fuel oil was taken to determine whether any of the POHCs selected in the waste were also present in the fuel oil. Using the same rationale, quench water samples were also taken for POHC analysis. These two streams (fuel oil and quench water) are not directly required by the trial burn protocol; but to establish input of POHCs, one needs to sample and analyze these streams for the selected POHCs. Table 1 shows the test matrix used in the trial burn at the MSD facility and is complementary to Figure 1 with respect to sampling points, number of samples taken per test day and the resulting number of samples, and the analyses carried out on the samples.

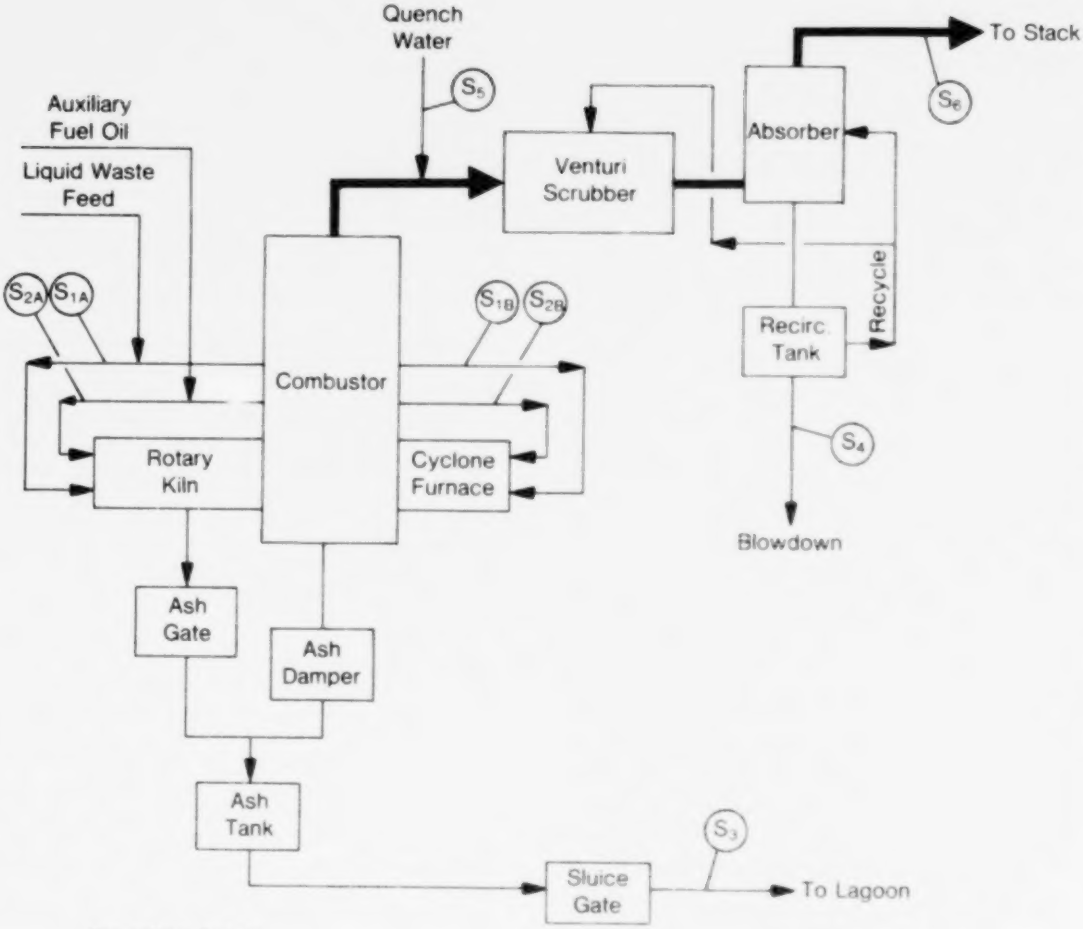
A few additional points should be made with regard to Table 1 which bring out the ambiguities in the protocol. The first one deals with the duration of the trial burn. It is not clear from Reference (1) what the duration should be. For purposes of this program, we chose a 6-day duration for the trial burn based on three operating temperatures and two residence times. The operating temperatures and residence times were selected to provide a good range to evaluate DRE as a function of both parameters. Also, an 8-h test day was chosen. Secondly, the EPA guidance document does not prescribe stack sampling times. Since sampling time is related to the concentration of POHC in the waste, the expected concentration of the same POHC in the stack, and the detectability of the analysis procedure, we thought it prudent to conduct stack sampling for both a 2-h period and a 6-h period. The 2-h sampling time corresponds to the EPA Method 5 requirement, and the 6-h period was chosen to enable collection of a sufficient quantity of POHC if it was present at the 100-ppm level in the waste and was destroyed at the 99.99%-level. These two sampling times would provide a better perspective for selection of sampling durations in future trial burns.

Waste sample collection times or intervals are also not well prescribed. Since industrial waste is often nonhomogeneous, one must ensure that the waste characterized is indeed the waste that is burned throughout the trial burn. To address this aspect we took, as shown in Table 1, grab samples of waste as well as integrated samples over the 2-h period and the 6-h period corresponding to the 2-h and 6-h stack sampling times.

The sampling train used during the trial burn is shown in Figure 2. This train is similar to that used for capturing organic emissions from various emission sources. The XAD resin and the two impingers downstream of the resin enable capture of POHCs, and the impinger containing silver-catalyzed solution is for capture of volatile metals, viz As, Se, and Hg. Due to the high moisture content in the stack, we used a 4-liter bottle downstream of the XAD resin instead of the regular impinger, shown in Figure 2, for a second set of tests.

Many of the analysis procedures for POHCs and chlorides had to be developed as part of this program, since methods in Reference (1) were primarily based on analysis of organics in wastewater and could not be used here. In many of the samples we encountered two separate organic phases and a semisolid phase.

In all cases, the four components of each train (probe rinse, filter, XAD, and condensate) were extracted and then combined for POHC analysis by GC/MS so that DRE could be calculated for each POHC.



Sampling Points

S_{1A}, S_{1B} = Liquid Waste Feed
S_{2A}, S_{2B} = Auxiliary Fuel Oil
S_3 = Ash Sluicing
S_4 = Scrubber Blowdown
S_5 = Quench Water
S_6 = Stack

Figure 1. Schematic illustration of incineration facility with sampling points.

TABLE 1. TEST MATRIX FOR TRIAL BURN AT CINCINNATI INCINERATOR

- One liquid waste (5 POHCs to be selected)
- Three operating temperatures--899°C (1650°F), 1093°C (2000°F), and 1316°C (2400°F)
- Two residence times
- Total of six test days

Sampling point	No. of samples/test day	Total No. of samples/waste for six test days	Analysis
SIA/SIB Waste	Two 2-h integrated samples and one 6-h integrated sample	2 + 1	5 POHCs, 12 metals,* Cl^-, HHV, vis., F.P., prox/ult
	1 other grab once each day	6	
S_{2A}/S_{2B} Fuel Oil	1 grab (mainly to verify absence of POHCs)	6	5 POHCs, Cl^-
S_3 Ash	4 grab (one for each section of sluice tank when plant dumps ash)	24	5 POHCs, Cl^-
S_4 Scrubber Effluent	3 grab	18	5 POHCs, Cl^-
S_5 Quench Water	1 grab (mainly to verify absence of POHCs)	6	5 POHCs, Cl^-
S_6 Stack	· 4 EPA Method 5 trains (two simultaneous 6-h trains and two 2-h trains)	24	Particulate, metals (As, Se, Hg), 5 POHCs, 2 PICs
	· 2 chloride trains	12	Cl^-
	· 3 ORSAT runs for O_2 and CO_2	18	O_2, CO_2
	· Continuous monitoring for Co, O_2, NO_x, total HC	-	CO, O_2, NO_x, total HC
	· 1 integrated gas sample	6	5 POHCs

* Twelve metals analyzed were Ag, As, Ba, Be, Cd, Cr, Hg, Ni, Pb, Sb, Se, and Te.

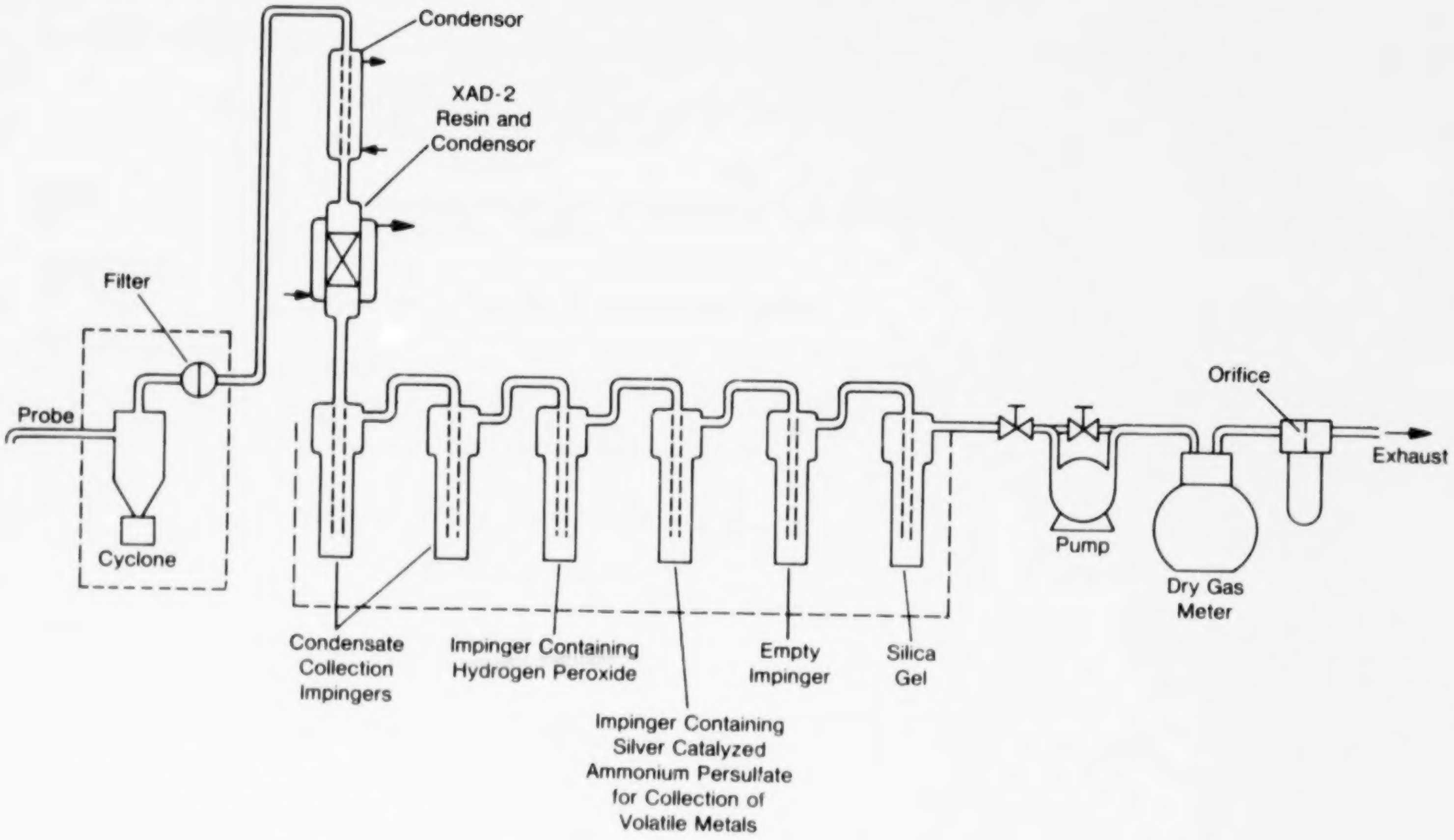

Condensor
XAD-2 Resin and Condensor
Filter
Probe
Cyclone
Orifice
Exhaust
Pump
Dry Gas Meter
Condensate Collection Impingers
Impinger Containing Hydrogen Peroxide
Impinger Containing Silver Catalyzed Ammonium Persulfate for Collection of Volatile Metals
Empty Impinger
Silica Gel

Figure 2. Sketch of sampling train used during tests.

To ensure that volatile POHCs were accounted for, we used integrated gas bag samples to collect stack gases for analysis, in addition to the sampling train itself. In a similar vein, additional analyses were carried out for the samples collected by the chloride sampling trains used at the stack. This was done because the sampling/analysis method suggested in Reference (1) measures total chlorides, whereas the regulation specifies 99% HCl removal.

In spite of the above difficulties, we successfully completed trial burns on two liquid wastes. Some of the available results of the first trial burn are presented below; other results will be discussed during the presentation of this paper.

Waste Analysis and Selection of POHC

Analysis results of the six 6-h integrated waste samples for all potential POHCs (both volatile and semivolatile) are shown in Table 2, in the order of their heat of combustion. This list is limited to those compounds present at 100 ppm or greater, since, as noted in Reference (1), detection of compounds present at < 100 ppm would present detection difficulties in the stack samples at a DRE of 99.99%.

From the list of POHCs in Table 2, the first four were selected for analysis in all samples. In addition, we recommended that hexachlorobenzene be included as one of the selected POHCs because of EPA's interest in this compound as a surrogate for PCB. We also recommended that hexachlorocyclopentadiene (HCCP) be included as another of the selected POHCs because it is present at relatively high concentrations in the waste (14,000 to 39,000 ppm). It is a pesticide of particular interest to the Cincinnati MSD and EPA. In summary, the six POHCs selected for analysis in all samples are carbon tetrachloride, hexachloroethane, chloroform, tetrachloroethene, hexachlorobenzene, and hexachlorocyclopentadiene.

Results of the metals analysis on the six 6-h integrated waste samples are shown in Table 3. The analysis data are presented for the liquid phases as well as the solid phase of each sample since the waste samples were biphasic and nonhomogeneous. The metals listed in Table 3 are those required by the protocol.

Destruction/Removal Efficiency (DRE) of Selected POHCs

Determination of DRE is of utmost importance in a trial burn. For the six POHCs selected, analytical results are available for both 6-h trains used in Runs 1, 2, and 3. Using these stack results and the results of the waste analysis, DREs have been computed for the six POHCs of interest. These DRE results are shown in Table 4.

These results show that the required 99.99% DRE was achieved for five of the six POHCs. The DRE for tetrachloroethylene was slightly below 99.99% in most of the tests. If one "rounds off" the results for this compound, it can be seen that in each run one of the simultaneous 6-h trains would show 99.99% while the other would show somewhat less (99.97 to 99.98%). Thus, further analyses of data from other runs will be needed to assess the precision of the sampling/analysis results.

Review of the data given in Table 4 indicates, somewhat surprisingly, that the DRE for each of the POHCs was unaffected by the combustion temperatures chosen for the tests (Run 1 - 899°C, Run 2 - 1093°C, and Run 3 - 1316°C). This, in effect, means that 899°Cis adequate to obtain high DREs for the POHCs selected.

More data on DRE will be reported at the meeting after review of all analysis data on the 2-h and 6-h trains.

Chloride Removal Efficiency

Chloride removal efficiency was based on analysis for chlorine in the waste feed and two HCl sampling trains operated on each test day. Results are given in Table 5.

The results show that there was only one test (2A) in which the required removal efficiency of 99% was achieved. However, as we have discussed, the

TABLE 2. ANALYSIS RESULTS AND RANKINGS FOR POTENTIAL POHCs (> 100 μg/g) IN 6-h INTEGRATED WASTE FEED SAMPLES

Rank	Hc*	100/Hc*	Compound	Concentration range[†] (μg/g)	Class[‡] V or SV
1	0.24	416.7	Carbon tetrachloride	1,600-9,800	V
2	0.46	117.4	Hexachloroethane	310-650	SV
3	0.75	133.3	Chloroform	2,000-12,000	V
4	1.19	84.0	Tetrachloroethene	1,300-1,800	V
5	1.70	58.8	Methylene chloride	1,000-7,300	V
6	1.74	57.5	Trichloroethylene	500-680	V
7	1.79	55.9	Hexachlorobenzene	120-260	SV
8	1.99	50.3	Trichloroethane	1,000-13,000	V
9	2.05	48.8	Pentachlorobenzene	< 100-110	SV
10	2.10	47.6	Hexachlorocyclopentadiene	14,000-39,000	SV
11	2.12	47.2	Hexachlorobutadiene	450-1,200	SV
12	3.00	33.3	Dichloroethane	1,000-5,100	V
13	3.38	29.6	Isodrin	2,000-2,700	SV
14	3.40	29.4	Trichlorobenzene	< 100-110	SV
15	3.75	26.7	Aldrin	180-300	SV
16	4.51	22.2	DDT	130-280	SV
17	4.57	21.9	Dichlorobenzene	1,100-5,100	SV
18	6.60	15.2	Chlorobenzene	1,600-4,600	V
19	6.92	14.5	Chlorotoluene	1,200-1,700	SV
20	7.34	13.6	Di-n-butylphthalate	100-180	SV
21	7.78	12.9	Phenol	100-3,800	SV
22	8.07	12.4	Toluene	3,100-5,100	V
23	8.07	12.4	Methyl ethyl keton	1,600-3,700	V
24	8.29	12.1	Butylbenzylphthalate	< 100-150	SV
25	8.42	11.9	Bis(2-ethylhexyl)phthalate	100-2,300	SV
26	8.51	11.8	Dimethylphenol	150-560	SV
27	9.62	10.4	Naphthalene	680-1,600	SV
28	10.03	10.0	Benzene	200-1,000	V

* H_c = Heat of combustion in kcal/g.

[†] Concentration range shown is the lowest and highest concentration found in the six 6-h integrated waste feed samples.

[‡] Class designates whether the compound is a volatile (V) or semivolatile (SV). This designation reflects the analysis techniques for the waste feed samples and the fact that, subsequently, volatiles will most likely be detected in the integrated gas bag samples while semivolatiles will most likely be detected in the modified Method 5 train samples.

TABLE 3. RESULTS OF METALS ANALYSIS ON WASTE FEED SAMPLES (μg/g)*

Metals	Run 1		Run 2		Run 3		Run 4		Run 5		Run 6	
	Liquid	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid
Ag	< 0.004	2.8	0.2	2.8	< 0.02	1.9	< 0.004	2.5	< 0.02	1.2	< 0.02	1.9
As	4.5	35	3.0	20	6.0	30	3.5	30	6.5	5.5	6.4	27
Ba	0.4	2,200	0.5	3,600	0.7	1,600	0.6	1,300	0.5	310	0.6	1,200
Be	0.02	3.0	< 0.0002	< 0.01	< 0.0002	0.3	0.01	< 0.2	< 0.0002	< 0.01	< 0.0002	0.01
Cd	24	100	29	80	11	55	28	60	11	60	6.5	50
Cr	69	2,400	65	2,400	84	2,100	86	2,400	83	2,400	76	1,900
Hg	1.2	14	0.6	15	1.2	13	1.0	15	1.3	4.3	1.3	12
Ni	16	70	15	45	8.1	86	14	140	7.7	110	5.0	160
Pb	550	10,000	630	11,000	550	7,900	920	89,000	390	800	600	1,700
Sb	28	230	31	420	18	130	30	270	14	70	15	170
Se	6.3	30	5.5	< 9	4.4	35	5.2	45	3.6	30	3.2	20
Te	1.0	440	1.5	3.3	2.1	30	1.5	25	2.0	2.3	2.1	25

* Ratio of solids to liquid in samples was not determined but was estimated to be greater than 1% but not more than 10% of the liquid.

TABLE 4. SUMMARY OF DRE RESULTS

POHC	Run 1		Run 2		Run 3	
	M5(6)-1A	M5(6)-1B	M5(6)-2A	M5(6)-2B	M5(6)-3A	M5(6)-3B
Chloroform*	99.994	99.994	NA†	NA†	99.9991	99.9993
CCl*	> 99.999	> 99.999	NA†	NA†	> 99.9998	> 99.9999
Tetrachloroethylene	99.984	99.989	99.980	99.987	99.974	99.990
HCCP‡	99.99998	99.99998	99.99994	99.99998	99.99998	99.99999
Hexachloroethane	> 99.997	> 99.996	> 99.995	> 99.995	> 99.997	> 99.998
Hexachlorobenzene	> 99.993	> 99.992	> 99.991	> 99.991	> 99.994	> 99.995

Note: M5(6)-1A - Denotes modified Method 5, 6-h sampling train from Run 1; the A represents one of the two simultaneous trains.

* Results for chloroform and carbon tetrachloride, which are "volatile," are based on analysis of integrated gas bag samples. All others are based on analysis of modified Method 5 trains.

† The integrated gas bag from Run 2 developed a leak, so there was insufficient sample for analysis.

‡ HCCP = Hexachlorocyclopentadiene.

TABLE 5. SUMMARY OF CHLORIDE REMOVAL EFFICIENCY DATA

Run No.	HCl test No.	Cl in waste feed (%)	Chloride removal efficiency (%) Total	Excluding plug
1	1A	2.96	95.4	97.7
1	1B	5.76	97.8	99.7
2	2A	9.23	99.0	99.8
2	2B	10.09	98.9	99.7
3	3A	2.97	96.2	99.4
3	3B	6.92	98.4	99.8
4	4A	6.24	97.8	99.5
4	4B	5.76	86.1	98.2
5	5A	9.60	95.9	98.6
5	5B	8.86	94.8	99.0
6	6A	11.16	97.9	99.8
6	6B	11.16	32.0	80.0

TABLE 6. SUMMARY OF PARTICULATE DETERMINATIONS

Run No.	Train No.	Particulate concentration g/dscm (gr/dscf)	g/dscm (gr/dscf) corrected to 12% CO_2
2	M5(2)-2B	0.2124 (0.0928)	0.3272 (0.143)
5	M5(2)-5B	0.0819 (0.0358)	0.1467 (0.0641)

regulations require 99% HCl removal, whereas the sampling method measures total Cl emissions. Thus, if there is any mist or droplets of the scrubbing solution in the stack, they will probably be captured by the glass wool "plug" used in the front of the HCl sampling probe, according to the method specified in Reference (1). For this reason, Table 5 also shows HCl removal when excluding the Cl determined in the plug component of the sampling train. In all tests contribution of the plug to the total was quite large.

Exclusion of the plug shows that the 99% removal efficiency requirement was met in 8 of the 12 runs. In order to investigate the possibility that carryover of scrubber solution was causing the low removal efficiency, components of the sampling train are presently being analyzed for sodium.

It was noted that there seemed to be considerable variability in the chlorine level in the waste feed samples. This is presently being investigated.

Particulate Emissions

Two 2-h modified Method 5 trains were used during each test, which resulted in a total of 12 trains. Since these were primarily intended for POHC analysis, only two of these trains were utilized for determination of particulate catch. This involved evaporation and weighing of the probe rinse and desiccation and weighing of the filters. Results of these particulate determinations are summarized in Table 6.

It can be seen in Table 6 that the corrected particulate concentration for Run 2 exceeded the RCRA limit of 0.183 g/dscm (0.08 gr/dscf), while the concentration in Run 5 was below the limit. However, neither of the above particulate data is considered very reliable since it was obvious that the fiberglass-packed sound dampeners in the stack were deteriorating rapidly and pieces of the fiberglass were being emitted from the stack and were interfering with the sampling probes.

REFERENCES

1. Guidance Manual for Evaluating Permit Applications for the Operation of Hazardous Waste Incinerator Units, prepared by the Mitre Corporation as a draft document under EPA Contract No. 68-01-6092, April 17, 1981.

ACKNOWLEDGMENTS

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EVALUATION OF POTENTIAL VOC SCREENING INSTRUMENTS

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ABSTRACT

This paper describes the evaluation of potential fugitive source emission screening instruments for analysis of volatile organic compounds (VOC). An initial review of available portable VOC detection instruments indicated that detectors operating on several principles (i.e., flame ionization, catalytic combustion, photoionization, infrared absorption, and thermal conductivity) might be useful for VOC analysis. However, flame ionization and catalytic combustion devices evaluated previously have shown poor sensitivity for highly substituted aliphatic and aromatic organic compounds. Instruments operating on the photoionization and infrared principles may be able to meet necessary criteria for practical and accurate VOC analysis of highly substituted organics. Therefore, three commercially available instruments were selected, modified, and evaluated for 32 such compounds in the concentration range of 100 to 10,000 ppmv. The results indicate that the photoionization principle may be suitable for general VOC screening but a reliable instrument/dilution system does not exist at present. The infrared absorption principle will apparently not provide a suitable general VOC screening device but may be useful for analysis of some classes of organic compounds.

INTRODUCTION

The U.S. Environmental Protection Agency has issued guidelines (6) for volatile organic compounds (VOC) from several stationary source categories such as surface coating operations. These guidelines are for industries which emit significant quantities of air pollutants. It has become apparent that sources other than classical point sources may also emit VOC's into the workplace and surrounding atmosphere. The EPA's Office of Air Quality Planning and Standards (OAQPS) is, therefore, evaluating the need for the control of fugitive emissions of VOC's, from such sources as valves, pumps, and drains. As described in EPA Method 21, Determination of Volatile Organic Compound Leaks (7), technically and economically feasible devices suitable for monitoring such leaks include only a few portable detectors. These devices can be placed near possible points of emissions and will respond to releases of the organic compounds. Specific instruments suitable for this purpose include, but are not limited to, catalytic oxidation, flame ionization, infrared absorption, and photoionization detectors.

Unfortunately, due to the chemical complexity of many fugitive sources and the lack of universal sensitivity of these detectors, the detectors previously evaluated cannot adequately measure all the volatile chemicals likely to be released. This fact has been documented (2) for two commercially available detectors using flame ionization (FID) and catalytic combustion principles. Among 168 compounds tested, 23 showed sufficiently poor response that the actual and measured concentrations differed by a factor of greater than five (Table 1). The classes of compounds which show the poorest agreement with the actual concentration generally incorporate functional groups such as halides, hydroxyls (alcohols), carbonyls (aldehydes, ketones), and carboxylates (acids) and include both substituted aromatic hydrocarbons and low molecular weight, highly substituted aliphatic compounds.

Additional portable devices which respond accurately to these compounds are needed for VOC screening. Instruments other than flame ionization or catalytic oxidation detectors which might meet this goal operate on the principles of infrared absorption, photoionization, and thermal conductivity (1).

The first step in this task was to select and procure one or more units of those detectors which meet the mechanical specifications of Method 21 (7). The VOC instrument had to be rugged, reliable, relatively inexpensive, portable, and easy to operate. The instrument had to be intrinsically safe for operation in explosive atmospheres as defined by the applicable National Electric Code. Of course, it had to respond to the organic compounds of interest and be able to measure the leak definition concentration specified in the regulations. At this time, few

TABLE 1. COMPOUNDS WITH RESPONSE FACTORS EQUAL TO OR GREATER THAN FIVE

OCPDB* ID No.	Compound Name	FID Response Factor#
120	Acetophenone	10.98
--	Acetyl-1-propanol,3-	10.87
490	Benzoyl Chloride	6.40
790	Carbon Disulfide	571.92
810	Carbon Tetrachloride	21.28
830	Chloro-Acetaldehyde	13.40
--	Dichloro-1-propanol,2,3-	61.51
--	Dichloro-2-propanol,1,3-	29.34
--	Diisopropyl Benzene,1,3-	9.43
--	Dimethyl Styrene,2,4-	37.09
2060	Formic Acid	34.87
1221	Freon 12	9.65
2073	Furfural	7.96
2105	Glycidol	8.42
--	Hydroxyacetone	8.70
2500	Methanol	5.69
--	Methyl-2,4-pentanediol,2-	96.34
2690	Methylstyrene, α-	10.24
1660	Monoethanolamine	28.04
2770	Nitrobenzene	29.77
2910	Phenol	11.75
--	Phenyl-2-propanol,2-	89.56
3291	Tetrachloroethane,1,1,2,2-	6.06

*Organic Chemical Producers Data Base

$$^{\#}\text{Response Factor} = \frac{\text{Actual Concentration}}{\text{Measured Concentration}}$$

Source: (2)

detectors are "approved."

The second step in this task was to set up a laboratory system capable of mixing known volumes of vapors with air and delivering the mixtures of known concentration to the detectors. Tedlar bags and a volumetric mixing system were selected for sample preparation since they provide adequate accuracy/precision and require little cost or time to set up.

The third step in this task was evaluation of the detectors for response to the compounds of interest. The response factors were determined at several concentrations over the range of 100 to 10,000 ppmv. Measurements were limited to concentrations approaching about 90% of the saturation concentration or 75% of the lower explosive limit (LEL). In order to permit statistically valid interpretation of the measured response factors, five replicate measurements at three concentrations were conducted. Data analysis included calculations of mean response factors and confidence intervals.

Subsequent to this evaluation, a photoionization detector attached to a gas chromatograph was utilized to independently confirm the resonse factors observed with the portable detectors. This step provided appropriate quality assurance and expanded the available data base.

INSTRUMENT SELECTION

General Rationale

A recent summary of available portable VOC detection devices (1) lists a number of instruments operating on the following principles:

Flame Ionization (FID)
Photoionization (PID)
Infrared Absorption (IR)
Thermal Conductivity (TC)
Hot Wire/Catalyst Combustion
(Combustion)

The majority of available instruments operate on one of three principles; i.e., FID, IR, or Combustion (1). As noted previously (2), two specific FID and Combustion devices were shown to have poor sensitivity to several substituted organic compounds. Due to this observation and with the assumption that other FID or Combustion detectors available from different manufacturers probably do not differ significantly in their basic response factors, alternative VOC screening devices were evaluated. These were selected from instruments operating on other detection principles, including PID, IR, and TC (1).

The selection of potential VOC detectors from this list depends on several criteria which are outlined in EPA Method 21. That is, an instrument suitable for screening should have the following characteristics:

1. Fast response (<30 seconds);
2. Measurement range 100 to 10,000 ppmv;
3. Similar responsiveness to a variety of organic vapors;
4. Portable;
5. Rugged;
6. Reliable;
7. Inexpensive;
8. Easy to operate; and
9. Intrinsically safe (as per National Electric Code).

Each of the first three characteristics is of primary importance in providing a practical instrument for VOC screening. Fast response time is necessary for rapid screening of a large number of fugitive sources. The specified measurement range is required by the need to limit significant leaks of VOC's.

Equal molar sensitivity to compounds of widely differing functional character is not achievable with currently evaluated instruments but is a desirable goal. The other characteristics, such as portability and intrinsic safety, are also important but none should be considered individually critical to the acceptance of a potential detector.

Assuming that characteristics of fast response and appropriate measurement range are available in potential VOC detectors, the ability of the devices to meet the criterion of similar responsiveness needs to be reviewed prior to final instrument selection. Thus, the efficacy of various operating principles to meet this criterion is discussed below.

Photoionization detectors utilize ultraviolet radiation to ionize a small fraction of molecules introduced into an ionization chamber. The ionization process is initiated by absorption of a photon of sufficient energy (i.e., greater than the ionization potential) to remove an electron from its ground state to infinity. A free electron and positively charged ion are thus formed:

$$R + h\nu \rightarrow R^{+} + e^{-}$$

If the energy of the UV lamp is less than the ionization potential of the compound, no ionization takes place. Ions formed in the detector/ionization chamber may reach the electrodes under the influence of an electric field and produce a small current. The number of ions which reach the electrode is proportional to the concentration, although only a very small fraction (~0.01%) of the molecules in the ionization chamber are ionized by incident radiation. Depending on the character of the electrons (e.g., sigma vs pi electrons) the yield of ions (photoionization efficiency) may vary as a function of the energy of incident photons. At present, UV sources are available for commercial instruments which emit photons of approximately 9, 10, or 12 eV. Based on the ionization potentials of organic compounds (5), it is apparent that certain classes of compounds (e.g., aromatics and aliphatics greater than carbon number C7) can be ionized by a 10 eV lamp while many substituted aliphatics require photons of at least 11 eV. This observation leads to the conclusion that with sufficient energy most organic compounds can be ionized and detected. A practical upper energy limit for VOC analysis is about 12 eV since the major components of air (such as nitrogen, carbon monoxide, carbon dioxide, and water) have ionization potentials above this level. As well as the ionization potential, the photoionization efficiency is important since this parameter determines sensitivity of the technique to different compounds. A recent paper (4) indicates that the molar sensitivity of aliphatic and oxygenated aliphatic compounds is several times less than that of aromatic compounds if incident radiation is about 10.2 eV. In fact, for aliphatic hydrocarbons of carbon number less than C8, the relative sensitivity is less than one-tenth that for benzene. If incident radiation is about 11.7 eV, the relative sensitivity of aliphatic and aromatic compounds is similar (3) and perhaps within a factor of two. Based on this assumption, a commercially available photoionization instrument with a lamp of about 12 eV may provide a generally applicable VOC detection technique.

Typical nondispersive infrared devices operate by passing infrared radiation through two separate absorption cells: a reference cell and a sample cell. The sealed reference cell is filled with nonabsorbing gas, such as nitrogen or argon. The sample cell is physically identical to the reference cell and receives a continuous stream of gas being analyzed. Subsequently, the net radiation in the two beams are passed into and absorbed in matched selective detectors (e.g., Luft detector) containing the vapor to be detected. When organic vapors are present in the sample cell, energy is absorbed, and the temperature and pressure in the corresponding detector is reduced relative to that in the detector on the reference side of the analyzer. A diaphragm between the two detectors is displaced and the amount of displacement is detected, electronically amplified, and an output signal proportional to concentration produced. In other NDIR systems, narrow bandwidth filters which pass energy which corresponds to that absorbed by the compound of interest are used along with simple solid state IR detectors. In both cases, interference from compounds with overlapping absorption bands is possible. More importantly, the maximum absorbing wavelength for different organic species in the sample gas may not correspond to the maximum absorbing wavelength of the calibration compound used in the detector. Within reason, several different calibration compounds could be used in the detector to improve responsiveness for several compounds. Alternatively, by selection of a single narrow bandwidth filter with a wavelength corresponding to a general aliphatic C-H stretch, many aliphatic hydrocarbons might be detected quite uniformly. Based on the maximum absorption wavelength of aromatic hydrocarbons, a separate filter or cell would be needed for this class of compounds. In practice, the specificity of the detection principle has precluded the manufacture of an NDIR device suitable as a general (i.e., both aliphatic and aromatic) organic vapor detector.

An alternative IR detection scheme involves dispersive IR analysis in which the specific wavelength absorbed by the organic vapor of interest is passed through a single sample cell. In this case, selectivity is provided by a monochromatic light source rather than a selective detector. Such a device is inherently more selective than an NDIR and thus may be less appropriate as a VOC screening device. However, by successive, rapid monitoring of IR absorption at several selected wavelengths corresponding to the maximum absorption wavelengths for several organic functional groups (e.g., aliphatic CH, aromatic CH, C-Cl, C=O), it may be possible to identify and quantify a wide variety of organic vapors in a fugitive emisson source.

Unit Selection

On the basis of the factors discussed above, both the IR and PI principles might be suitable for general VOC screening. However, a comparison of the specifications of commercially available instruments operating by these principles and the criteria of Method 21 leads to a rather unfortunate conclusion: No instruments of these types are adequate for screening of VOC emissions. In terms of a desire to expand the list of potential detectors, such a finding is unsatisfactory.

What criteria led to this finding? The most obvious answer is the requirement for an intrinsically safe device. No IR or PI devices are certified for use in Class I, Division 1 environments. One PID is certified for use in Class I, Division 2. It should be noted, however, that in the future other devices may be modified so as to meet Class I, Division 1 certification. Alternatively, the use of an instrument only in less hazardous environments may not be considered as particularly restrictive. For these reasons, the criterion of intrinsic safety was given lesser significance and not used to rule out potential devices for screening in this program.

The other criteria listed previously were ranked in approximately descending order of importance for field application. Thus, a response time of less than 30 seconds was given the highest importance. In fact, fast response time is very important to practical measurement of VOC leaks, and several instruments with faster than 30-second response time are availabile. Thus, it was decided that this criterion must be met by any instrument to be evaluated. The criteria of portability, ruggedness, and ease of operation are also important but were not chosen as absolute selection criteria. Portability can be evaluated subjectively, and devices operated with automobile batteries placed on a small cart may be considered to have adequate portability. Devices operated with AC power are less practical in many industrial environments.

Current literature and additional manufacturers' information were reviewed using the modified criteria described above. A list of potential VOC detectors was developed (Table 2). This list includes instruments which operate on PI and IR principles and which meet most of the Method 21 criteria. It is obvious that not all of the IR instruments that meet most of the criteria are included. Since the goal of this study is to evaluate the usefulness of the IR principle rather than all available IR devices, only selected IR devices suitable on the basis of the criteria for VOC screening were included.

The list, therefore, includes a dispersive IR device and NDIR devices with or without solid state detectors. The NDIR devices may be useful for a specific group of organics; e.g., aliphatic hydrocarbons. Also included are two devices operating on other detection principles; i.e., ion capture and UV spark. These instruments are only useful for a specific class of organics (i.e., halogenated hydrocarbons) but were included due to the widespread industrial use of these solvents.

The final instruments selected for evaluation were:

Instrument	Principle of Operation
AID Model 580	Photoionization
HNU PI-101	Photoionization
Foxboro Miran 80	Dispersive Infrared

The rationale for the selection of these instruments is based on both suitability and availability. As noted previously, PI may be a particularly suitable VOC detector for aliphatic, aromatic, and substituted organic vapors. Either of the commercially available, portable instruments meets most Method 21 criteria and may be suitable for evaluation.

TABLE 2. POTENTIAL VOC DETECTORS (1)

Instrument	Principle	Range (ppm)	Response (s)	Wgt (lb)	Pump	Power	Intrinsically Safe
ANARAD, Inc. AR-400 <5μm	IR	100-10,000	5	24	Yes	AC	No
Foxboro, Inc. Miran 80	IR	ppm → %	1-40	32	Yes	Car Battery (37 lb)	No
Foxboro, Inc. Miran 103	IR	ppm → %	1-40	23	Yes	AC	No
Infrared Industries IR-711 <5μm	IR Solid State	1000 100% LEL*	5-120	9	Yes	Battery	Yes
AID, Inc. 580	Photoionization	0-200, 0-2000	2	8	Yes	Battery	Pending
HNU Systems, Inc. (PI-101)	Photoionization	0-20, 0-200 0-2000	5	9	Yes	Battery	Yes
General Electric (TVM 1)	Ion Capture (Halogenated)	0-1 → 0-10,000	120	23	Yes	No	No
Gas Tech, Inc. (Hal[illegible])	UV Spark (Halogenated)	0-100, 0-10,000	5	13	Yes	AC	No

*LEL ≡ Lower Explosive Limit

The Miran 80 instrument is the one available infrared device which permits a selection of wavelength as opposed to selection of a test compound in a reference cell. This option permits the rapid (a few seconds) assessment of the suitability of several wavelengths for the measurement of the substituted organics of interest. Specific examples are an aliphatic C-H stretch, aromatic C-H stretch, or a C=O stretch. Other portable IR devices utilize a filter at one specific wavelength band corresponding, for example, to an aliphatic C-H stretch. Thus, they have an inherent selectivity against aromatic or substituted species. Since all three classes of compounds are of interest, the latter devices are not preferred as VOC screening devices. It is possible that one wavelength may be suitable for analysis of a wide variety of organic vapors. If that is the case, other IR instruments could potentially be used for VOC leak detection. In summary, the Miran 80 (with associated microprocessor) permits the most rapid and cost-effective assessment of the IR principle as a general VOC detector. Other IR devices were, therefore, not evaluated.

The halocarbon specific detectors (i.e., General Electric TVM 1 and Gas Tech Halide Detector) were not selected for evaluation despite the potential usefulness of such a device in environments subject to halocarbon solvent contamination. Neither the GE TVM 1 nor an equivalent model is now sold. The Gas Tech device could not be modified to meet the intrinsic safety requirements of Method 21 due to the presence of a spark in the detector section.

No other instruments appeared to have a reasonable expectation of meeting the Method 21 criteria and of providing a significantly different performance than those devices evaluated previously or selected for evaluation in this study.

Unit Modifications

Both photoionization devices operate with a maximum quoted linear range of 0-2000 ppmv. In fact, the linear range is frequently reported to be only about 0-1500 ppmv. Since the maximum concentration of concern in VOC screening is 10,000 ppmv, dilution of sample air is necessary for both instruments to operate in the linear range. Both HNU Systems, Inc. and AID, Inc. provided their instruments with dilution systems designed in their respective laboratories. The HNU Systems, Inc. design consisted of (1) a fine bore restrictor which limited the flow of sample air and (2) a charcoal tube which passed an excess (10x) of hydrocarbon-free air (methane is not removed but does not respond in the detector). The sample stream is thus diluted about 1 to 10. The AID, Inc. design consisted of a pump and needle valve which diverted 90% of the incoming sample air through a charcoal tube and 10% to the normal exhaust point. The hydrocarbon-free (except for methane) sample air is combined with the incoming sample stream and thus a continuous tenfold dilution is provided.

Problems were observed with these dilution systems and the UV lamps provided with both instruments. The absolute accuracy of the dilution ratios is in some doubt since independent flow rates were difficult to measure. The UV lamps provided with both instruments were subject to degradation during the life of the study. In fact, the 11.8 eV lamp supplied with the AID, Inc. device failed during the study and, unfortunately, a replacement could not be obtained in time to collect useful data with this instrument. The 11.7 eV lamp supplied with the HNU Systems, Inc. device failed during the study and a replacement was provided. The difference in energy output from the two HNU Systems, Inc. lamps was large (i.e., a factor of three to ten depending on the age of the lamp). This variation affected the linear range of the instrument and created problems in obtaining consistent results. In some cases with the new lamp, saturation of the detector occurred even with the dilution probe attached to the instrument. The test results reported must, therefore, be carefully interpreted and conclusions narrowly drawn.

The Miran 80 operates over the concentration range from ppm to percent. The wide dynamic range is provided by a cell in which the pathlength of IR radiation can be changed by optical folding of the incident beam. At the concentration range of interest (i.e., 100 to 10,000 ppmv), the incident beam traversed a distance of about 0.75 m. At this pathlength, the full-scale absorbance for vapors of interest at a concentration of 10,000 ppmv was about 1 absorbance unit. Once the cell pathlength was set, no other modifications of operating conditions were required.

COMPOUND SELECTION

As noted in the Introduction, 168 compounds had previously been tested for response factor on two commercially available VOC detectors (2). Twenty-three showed sufficiently poor response that the actual and measured concentrations differed by a factor of greater than five (Table 1). The classes of compounds showing poor agreement were generally highly substituted aliphatic and aromatic compounds and those compounds incorporating functional groups such as carbonyl and hydroxyl groups. These 23 compounds were selected for testing on the alternative VOC screening devices to be evaluated in this study. Several other compounds, which were not evaluated in the previous work, were added to the list.

These compounds include only a portion of those commonly used in chemical production. At the request of OAQPS, other industrial compounds which have a vapor pressure greater than 0.3 kPa but which were not considered previously were reviewed. This extensive list of 76 compounds includes many species for which an FID or catalytic combustion detector would respond well. However, others are highly substituted compounds which will probably not give adequate response on these two detectors. Selected substituted compounds from the list were included in the detector evaluation.

The selection criteria required a response to several questions:

1. Are subsequent groups present or absent? If absent, don't test,
2. Are the compounds similar (functionally and/or isomerically) to others previously evaluated? If they are, don't test,
3. Are response factors on an FID instrument likely to exceed five? If not, don't test, and
4. Do the compounds pose a serious health hazard to laboratory personnel? If they do, cautiously consider evaluation.

As a result of the responses, the compounds were separated into two groups: compounds that should and those that need not be analyzed. Within the first group, the compounds were prioritized on the basis of (1) their similarity to other vapors to be analyzed (for example, positional isomers of compounds selected for testing were given lower priority), and (2) their health hazard (extremely toxic compounds with little commercial application or likelihood of release and which require complex/expensive handling were given lower priority).

The compounds selected for evaluation in this program are listed in Table 3. They are listed in the approximate order of testing.

EXPERIMENTAL PROCEDURES

Determination of response factors required initial calibration of the VOC detectors with a gas or gases of known concentration. Methane had been used previously for calibration of FID and combustion analyzers (2). However, the PID's do not respond to this compound, and the multiple wavelength analysis by dispersive IR spectrometry cannot be carried out by the use of methane as a single calibration gas.

Therefore, 1,2-dichloroethane was selected as the calibration gas for the PID's. This compound can be detected by the instruments and it has a response factor of about one (compared to methane) when analyzed on an FID. As a result, data collected in this study may be comparable to data collected in a previous EPA study (2).

Several calibration compounds were used for the IR evaluation since several wavelengths were scanned in the dispersive IR instrument to determine if any wavelength gave similar response factors for all the compounds of interest. The wavelengths were selected to correspond to key functional groups of the test compounds to be analyzed. The wavelengths, functional groups, and calibration compounds are listed in Table 4.

Once calibrated, the instruments were

TABLE 3. COMPOUNDS FOR EVALUATION

Carbon Disulfide
Carbon Tetrachloride
Chloro-Acetaldehyde
Dichloro-1-propanol,2,3-
Dichloro-2-propanol,1,3-
Diisopropyl Benzene,1,3-
Dimethyl Styrene,2,4-
Formic Acid
Freon 12
Methanol
Methylstyrene, α-
Tetrachloroethane,1,1,2,2-
Ethanol
Formaldehyde
Ethylene Dichloride (Dichloroethylene)
Chlorinated Ethanes (C_2H_5Cl, etc.)
Chlorinated Methanes (CH_3Cl, etc.)
Acetophenone
Benzoyl Chloride
Furfural
Monoethanolamine
Nitrobenzene
Phenol
Acetyl-1-propanol,3-
Glycidol
Hydroxyacetone
Methyl-2,4-pentanediol,2-
Phenyl-2-propanol,2-
Aniline Hydrochloride
Difluoroethane
Diketene
Dimethylsulfide
Glyceroldichlorohydrin
Paraldehyde
Perchloromethylmercaptan
Propylene Chlorohydrin
Toluenesulfonic Acid
Toluene Sulfonylchloride
Ethylene Glycol Dimethyl Ether
Ethylene Glycol Monoethyl Ether Acetate
1-Pentanethiol
Acetal
Chlorobenzoylchloride
Chlorodifluoromethane
Chlorotrifluoromethane
Trichlorofluoromethane
Trichlorotrifluoroethane
Cyanoacetic Acid
Neopentaneoic Acid
Amylmercaptans
    2-methyl-2-butanethiol
    2-methyl-1-butanethiol
    3-methyl-1-butanethiol
Glycols
    Ethylene Glycol Monoethyl Ether
    Ethylene Glycol Monomethyl Ether
    Ethylene Glycol Monomethyl
        Ether Acetate
Ethylene Glycol Monopropyl Ether
Glycol Methyl Ether (Dioxolane)

used to analyze the test compounds at three concentrations over the range of 100-10,000 ppmv. Details of the operation of each instrument are given in the manufacturer's instruction manual. During the tests, the lamp in Model 580 failed and a replacement could not be obtained. Therefore, only the PI-101 and Miran 80 were evaluated. The resonse factor was determined by calculating the ratio of the actual concentration to the concentration indicated by the instrument. The following paragraphs describe the procedures involved in calibration and operation of the instruments, preparation of test gas samples, and calculation of response factors.

Gas mixtures tested in this study were prepared in Tedlar gas sampling bags of a nominal 25 liter volume. These bags provide a relatively inert surface to preclude absorption, reaction, or permeation. They also permit visual inspection of the bag interior to provide an indication of sample condensation or reaction. The bags are equipped with two valves to facilitate flushing of sample gas and a septum to permit injection of sample liquid with a syringe.

Gas samples were prepared by the following procedure:

1. Flush and evacuate bag three times with hydrocarbon-free air (i.e., until no hydrocarbons are detected on each instrument).
2. Fill bag with 20.0 L of hydrocarbon-free air.
3. Inject a known volume of test compound into the bag.
4. Permit at least 1 hour equilibration to ensure adequate evaporation and mixing.
5. Draw gas sample from bag with each instrument.

The target concentrations prepared for

TABLE 4. CALIBRATION SCHEME FOR MIRAN 80

Wavelength (μm)	Functional Group(s)	Calibration Compound
3.3	Aromatic & Unsaturated C-H	Toluene
3.4	Saturated C-H	Pentane
3.6	Aldehyde C-H	Butyraldehyde
4.0	Reference Wavelength	Air
5.7	Carbonyl C=O	Acetone
6.35	Aromatic C-C, conj C=C (also N-H, C-S)	Toluene
8.8	Ether C-O-C	Diisopropyl Ether
9.5	Alcohol C-O-H	Isopropanol
13.5	C-Cl	1,2-dichloroethane

each compound were 500, 1000, 5000, and 10,000 ppmv. In several cases, it was not possible to prepare the higher concentrations due to the low vapor pressure of the compound or due to safety reasons; that is, such a concentration would exceed the lower explosive limit. In these cases, a concentration of 100 ppm was often prepared. For each target concentration, the required volume of liquid was calculated and measured in a microliter syringe.

Each instrument was initially calibrated (spanned) with a gas sample prepared in triplicate at a concentration of 10,000 ppmv. Calibration curves were then prepared by introducing samples of the calibration gas, prepared in triplicate at five concentrations over the range of 100 to 10,000 ppmv, into the instruments and recording the response. The PI-101 was calibrated with 1,2-dichloroethane while the Miran 80 was calibrated at individual analytical wavelengths with the compounds listed in Table 1.

During subsequent analysis of each test compound, the HNU PI-101 instrument was spanned with an 8040 ppmv 1,2-dichloroethane certified gas standard provided by Scott Specialty Gas, Inc. of Plumsteadville, PA. This span was carried out just prior to analysis of each set of sample bags for each test compound.

The Foxboro Miran 80 instrument was electronically zeroed and spanned according to the manufacturer's instructions. This zero and span check was carried out prior to analysis of each set of sample bags for each test compound.

The response factor reported in the following test results section is the number that, when multiplied by the apparent concentration based on instrument response, yields the actual concentration as calculated to exist in the gas bag sample. That is:

$$\text{Response Factor (RF)} = \frac{\text{Actual Bag Concentration (C)}}{\text{Concentration Calculated from Instrument Response}}$$

Response factors were determined at three actual concentrations; i.e., generally 100, 500, 1000, 5000, or 10,000 ppmv. No attempt was made to fit the three response factors for each compound to a particular function. For some compounds, the response factor is nearly identical for each concentration; whereas, for others it differs dramatically and in a complex manner. The response factor for individual compounds is, therefore, not reported for an observed instrument response of 10,000 ppmv. Instead, the mean response factors calculated from up to five replicate data points at each of the three actual bag concentrations are reported along with the standard deviation. Also reported is the 95% confidence intervals for the response factors as calculated from Student's t-test.

To provide additional quality control, expand the data base, and confirm response factors, HNU Systems, Inc. photoionization detector Model PI-51 was installed on a Varian 2800 gas chromatograph. Using an 11.7 eV lamp, solutions of specific organic compounds and toluene (reference compound) in several solvents were analyzed on a 3% SP 2250 on 100/120 Supelcoport column. Peak areas for the compound of interest and toluene were measured and relative detector sensitivities were determined on a molar basis and normalized against the detector response for toluene.

The molar sensitivity relative to toluene was calculated using the following equation:

$$RF = \frac{A}{A(tol)} \times \frac{B(tol)}{B}$$

where RF is the response factor,
A is the peak area of the compound of interest,
A(tol) is the peak area of the toluene peak,
B is the molar concentration of the compound of interest, and
B(tol) is the molar concentration of the toluene in the solution.

RESULTS AND DISCUSSION

Photoionization Detection

The photoionization technique was evaluated for a limited number of compounds due to both chemical and, more significantly, equipment problems. The PI-101 was calibrated with dichloromethane so as to permit direct comparison with response factors reported by Brown et al. (2). The response factors observed for the 16 compounds tested on the photoionization detector, PI-101, range from 0.50 to 48. Seventy-five percent (12) of the compounds have response factors of less than five and greater than 0.2. There appears to be no obvious trend of response factor with molecular weight (carbon number) or functionality within this group. On the other hand, it is interesting to note that both alcohols tested (i.e., methanol and ethanol) have response factors greater than five, and the values for methanol (C1) are higher than those for ethanol (C2). Thus, it appears that non-bonding electrons on the oxygen atom of the alcohols do not provide a much greater photoionization yield than other sigma-bonded electrons in compounds with similar carbon numbers. The high response factor for trichlorotrifluoroethane is consistent with its high ionization potential (11.78 eV). In fact, this ionization potential is slightly higher than the quoted energy of the UV lamp used in the study. This may indicate that thermal energy provides sufficient additional energy to permit some ionization when coupled to the energy provided by the UV light.

Although the specific response factors for the limited number of compounds tested do not unequivocally confirm the suitability of photoionization as a general VOC screening technique, an important but cautious observation can be made. That is, based on this small sample of compounds tested, which includes an aromatic compound (i.e., toluene), an ether (i.e., acetal), an alcohol (i.e., ethanol), and chlorinated alkanes (i.e., trichloroethane and chloroform), the response factor over a concentration range of 500 to 10,000 ppmv may be within a factor of five. This result is consistent with an expectation of more similar photoionization yields from sigma and pi electrons when the compound is influenced by UV radiation of approximately 12 eV rather than 10 eV. The expectation that photoionization yields for aliphatic and aromatic compounds may be similar indicates the potential usefulness of photoionization as a VOC screening tool.

In terms of current availability as a potential VOC detector, the most significant result with respect to the photoionization detector (HNU Systems, Inc. PI-101 and AID, Inc. 580) is probably the difficulty observed in operating the prototype dilution system. Both dilution probes were designed and fabricated by the respective manufacturers under severe time limitations. Neither probe was designed in a manner which permitted reliable independent measurement of dilution ratio or reproducible adjustment. Thus, the absolute dilution ratio is in some doubt. The ability to adjust the dilution ratios was practically nonexistent. As noted previously, the fixed dilution ratios were inappropriate for analysis of vapor concentrations which yielded instrument responses much above 10,000 ppmv or much below 1000 ppmv. Detector saturation was observed somewhat above an instrument response of 10,000 ppmv. At the span settings required for adequate operation, the background instrument response to zero air was quite high.

Whenever the intensity of the UV lamps began to decrease (note that the AID, Inc. lamp failed early in the program), the instrument span had to be increased regularly. Some alteration to the span potentiometer setting could be made to correct for this decrease in response. However, for some tests the correction was not sufficient to yield an identical calibration. Under these conditions, response factors were calculated at a different absolute instrument response. However, since the calibration curve is linear over the range of 0-10,000 ppmv (with dilution, that is about 0-1000 ppmv), no systematic error should occur due to the change in absolute response.

Due to declining instrument response and low vapor pressure of many compounds, half of the compounds tested did not yield reliable response factors. The problems noted above and limited data obtained indicate that, at the present time, a reliable photoionization system does not exist to operate over a VOC concentration range of 100 to 10,000 ppmv. More accurately, a reliable dilution/photoionization system is not available.

As noted previously, a comparison of response factors determined on the portable PI-101 analyzer and the PI-51 attached to a GC was conducted to independently confirm the accuracy of the data. The response factors for three chlorinated hydrocarbons listed below (Table 5) indicate good agreement (i.e., within ± 13%) on both instruments.

As a result of this agreement, the GC technique was utilized to effectively gather response factor data for homologues of several compound classes. Limited data have been attained (Table 6).

It is apparent that the response factor depends upon carbon number and functional character. For the three compound classes analyzed--aromatic hydrocarbons, halogenated aromatics, and chlorinated aliphatics--the response factor (relative to toluene) increases as the carbon number increases. Also, for the aromatic halides, the response factor increases as the electronegativity decreases.

Based on these observations it appears that a photoionization detector with an 11.7 eV lamp acts as a rough carbon counter and is able to respond to organic compounds with as few as one carbon atom and with significant substitution.

Infrared Detection

The results of the evaluation of the Miran 80 are more complete. A total of 32 compounds were analyzed. As noted previously, other compounds were not tested for several reasons, including (1) low vapor pressure; (2) reactivity; (3) lack of availability; and (4) close chemical similarity to compounds previously tested. Prior to testing, the instrument was calibrated with individual span gases at eight analytical wavelengths which correspond to individual functional groups; e.g., C-H, C-Cl, C-OH. The calibration curve data indicate that the absorbance values observed over the concentration range of 100 to 10,000 ppmv are linear. Test compounds were then run and the instrument response calculated on the basis of the response indicated by the specific span gas used at individual analytical wavelengths.

An analysis of the data indicates that the response factors for most compounds

TABLE 5. COMPARISON OF RESPONSE FACTORS FOR PHOTOIONIZATION DETECTORS

Compound	RF (PI-101) N=5	RF (PI-51) N=8	% Agreement
1,2-Dichloroethane	0.56	0.62	90.3
Methylene Chloride	0.37	0.40	93.3
Dichloroethylene	0.41	0.36	87.8

TABLE 6. RESPONSE FACTORS DETERMINED ON THE HNU SYSTEMS, INC.

PI-51 DETECTOR

Compound	Response Factor
Aromatic Hydrocarbons	
Benzene	0.49
Ethyl benzene	1.34
n-Propyl benzene	1.58
Cumene	1.30
n-Diisopropylbenzene	2.30
Halogenated Aromatics	
Fluorobenzene	0.60
Chlorobenzene	1.45
Bromobenzene	2.28
Iodobenzene	3.31
Chlorinated Aliphatics	
Dichloromethane	0.40
1,2-Dichloroethane	0.62
1,3-Dichloropropane	1.12
1,4-Dichlorobutane	1.54

with a particular functional group, determined at an analytical wavelength which corresponds to that functional group (Table 4), are generally less than a value of twenty. This is consistent with the general observation that the functional group is more important than the remainder of the molecule in determining the IR extinction coefficient of the compound at the wavelength of interest.

For example, three of the four aromatic compounds tested have reasonable response factors (less than five) at 6.35 μm as shown below. This wavelength is within a broad aromatic ring stretch area.

Compound	Response Factor Range
Diisopropyl Benzene	2.42 - 3.75
Dimethyl Styrene,2,4-	0.185 - 0.394
Methyl Styrene	0.229 - 0.718

Within this group, the addition of the large aliphatic group (isopropyl) on the benzene ring appears to reduce the sensitivity (larger response factor) at the aromatic C $\overset{\cdot\cdot}{-}$ C stretch wavelength as compared to less alkylated aromatics.

In the case of aliphatic and substituted aliphatic compounds, the C-H stretch wavelength of 3.3 μm yields suitable response factors (less than five) for about 52% of those tested. The classical aliphatic C-H stretch is observed at 3.4 μm, but some overlap of 3.3 and 3.4 μm IR bands may occur in the Miran 80 due to incomplete resolution. Also, some shift of the CH stretch wavelength probably occurs due to nearby oxygen or halogens. A list of aliphatic compounds and corresponding response factor ranges at this wavelength are shown in Table 7. If one includes alkylated aromatic compounds in the list of compounds with response factors less than five at 3.3-3.4 μm, the percentage of compounds tested with suitable response factors increases to 62%.

Ten chlorinated hydrocarbons tested in this program yielded measurable response factors at 13.5 μm. Seventy percent were observed to yield response factors less than five at this wavelength. The compounds and respective response factors are given in Table 8.

Since the ultimate goal of this instrument evaluation is to assess the suitability of IR as a general VOC screening technique, an assessment of the usefulness of a single wavelength for measurement of organic compounds of varied molecular weight and functionality is in order. A review of the data indicates that the number of test compounds (total of 32) which yield response factors of less than 20 or greater than 0.05 at each analytical wavelength is as follows:

Wavelength (μm)	Number of Compounds
3.3	23
3.4	12
3.6	13
5.7	17
6.35	17
8.8	11
9.5	25
13.5	14

In some cases, the response factors at a particular wavelength (e.g., 5.7 μm) are strongly a function of concentration. It appears that this may be due to a concentration broadening phenomenon which is frequently observed in gas-phase IR spectrometry. If only those compounds which show a response factor between 5 and 0.2, and those which show no strong variation in response factor with concentration (i.e., less than a factor of two from 1000 to 10,000 ppmv) are summarized as above, fewer compounds yield suitable response factors:

Wavelength (μm)	Number of Compounds
3.3	12
3.4	4
3.6	3
5.7	1
6.35	3
8.8	4
9.5	15
13.5	7

The results indicate that only 3.3, 9.5, and 13.5 μm analytical wavelengths respond acceptably for a large number of compounds (i.e., greater than 10% of the total number of compounds). However, in any case, fewer than 50% of the compounds are reliably detected. The aliphatic and aromatic compounds do not overlap at 6.35 μm but do overlap at 3.3 μm. However,

TABLE 7. SUBSTITUTED ALIPHATIC COMPOUNDS WITH RESPONSE FACTORS

LESS THAN TWENTY AT 3.3 μm

Compound	Response Factor Range
Acetyl-1-propanol,3-	1.23 - 2.02
Chloro-acetaldehyde	2.73 - 8.62
Dichloro-1-propanol,2,3-	18.5
Dichloro-2-propanol,1,3-	5.29
Diketene	8.06 - 14.1
Dimethylsulfide	0.488 - 0.495
Ethanol	0.261 - 0.292
Ethylene Glycol Dimethyl Ether	0.196 - 0.296
Ethylene Glycol Monoethyl Ether Acetate	0.280 - 0.488
Formaldehyde	1.09 - 1.88
Formic Acid	0.529 - 0.722
Glycidol	0.382
Methanol	0.294 - 0.410
Methylene Chloride	2.67 - 2.87
Pentanethiol,1-	0.314 - 0.633
Propylene Chlorohydrin	0.334 - 0.403
Tetrachloroethane,1,1,2,2-	8.59 - 9.90
Trichloroethane,1,1,1-	1.69 - 3.76

TABLE 8. CHLORINATED COMPOUNDS AND RESPONSE FACTORS AT 13.5 μm

Compound	Response Factor Range
Carbon Tetrachloride	0.233 - 0.302
Chloro-acetaldehyde	0.435 - 0.705
Chloroform	0.150 - 0.292
Dichloro-1-propanol,2,3-	0.431 - 0.538
Dichloro-1-propanol,1,3-	0.467 - 0.522
Methylene Chloride	0.0333 - 0.0840
Propylene Chlorohydrin	0.118 - 0.132
Tetrachloroethane,1,1,2,2-	0.0500 - 0.0990
Trichloroethane,1,1,1-	0.243 - 0.344
Trichlorotrifluoroethane,1,1,2-	4.41 - 4.55

note that only alkylated aromatics have good response at 3.3 μm. Thus, there is apparently no useful agreement in response factors between, for example, a large number of aromatic compounds and aliphatic compounds (e.g., 50% of those tested) at analytical wavelengths specific to each compound class. It is apparent that the overlap of IR absorbance bands of different functional groups is not sufficient to yield one analytical wavelength which might be used to quantify both compound classes with the expectation of agreement within a factor of five. This observation indicates that infrared spectrophotometry is not particularly suitable for general VOC screening.

On the other hand, the fact that the response factors do not vary by large values (i.e., greater than five) for some classes of compounds (e.g., halogenated aliphatics at 13.5 μm and aliphatic and alklyated aromatics at 3.3-3.4 μm) corroborates the suitability of IR spectrophotometry for VOC screening of compounds belonging to one functional group. Even in this case, only 30 to 80% of the compounds in a given class may yield response factors of less than five at a single specific IR wavelength.

CONCLUSIONS

In summary, based on the results of this evaluation, it appears that:

1. IR spectrophotometry is not suitable for general VOC screening, with the exception of analysis of VOC emissions of a single organic functional group character.
2. IR screening of organic compounds of a single functional class (e.g., C-Cl) may be suitable for as many as 80% of compounds in the class.
3. IR screening at a wavelength corresponding to both aliphatic and aromatic CH stretches may be suitable for as many as 30-50% of organic compounds.
4. A portable PID is not currently available for VOC screening in the concentration range of 100 to 10,000 ppmv.
5. The development of a reliable dilution probe for use on a PID is close at hand.
6. With such a dilution probe, it appears that a PID with an 11.7 or 11.8 eV UV lamp may be used for reliable analysis of VOC fugitive emissions.

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SURVEY METHODS FOR THE DETERMINATION OF PRINCIPAL ORGANIC HAZARDOUS CONSTITUENTS (POHCs)

I. Methods for Laboratory Analysis

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ABSTRACT

The U. S. Environmental Protection Agency (EPA) has established survey methods for the analysis of a specific list of priority pollutants. There are potentially other compounds whose presence or absence should be determined in analyzing incineration streams. To assess the applicability of EPA methods or similar survey methods to the determination of a broader range of principal organic hazardous constituents (POHCs), we have evaluated gas chromatography/mass spectrometry (GC/MS) and high-performance liquid chromatography (HPLC) methods for the determination of about 70 compounds (other than priority pollutants) from the list of POHCs.

The methods evaluated are presented, analytical results are given, and the potential applications of these survey methods are discussed.

INTRODUCTION

As part of the Resource Conservation and Recovery Act (RCRA), the U. S. Environmental Protection Agency (EPA) has promulgated interim final and proposed regulations for the owners and operators of facilities that treat hazardous wastes by incineration (4). The regulations cover a range of activities including operational performance standards, waste analysis, trial burns, monitoring and inspections, record keeping and reporting, and the establishment of emission control criteria. The specific details for each incinerator facility are authorized by facility permits.

As part of the supporting documentation for the permit writer and for the incinerator facility owners and operators, a manual of sampling and analytical methods (5) has been compiled by the EPA for use in measuring the levels of principal organic hazardous constituents (POHCs) in the various streams of an incinerator facility, including inlet wastes, stack gas, process waters, fly ash, and bottom ash. This manual, referred to as the "Methods Manual," expands upon and augments the information in Reference 7. The Methods Manual is intended to be a resource document for the preparation and execution of a sampling and analysis plan for hazardous waste incinerators. Existing collections of sampling and analysis methods documentation such as References 1 and 6 have not been directly incorporated into the Methods Manual, but are incorporated by reference.

Although the Methods Manual includes test procedures for proximate, survey, and directed (or specific-compound) analysis, the emphasis of our work was limited to directed analysis. The directed-analysis portion of the waste characterization scheme provides qualitative confirmation of compound identity and quantitative data with appropriate quality control for the potentially hazardous constituents that might reasonably be expected to be present in the waste, based on engineering judgment and on the results of proximate and survey analyses.

The Methods Manual recommends a variety of directed-analysis techniques for the determination of the list of POHCs given in Appendix VIII, Part 261, 40 CFR. Whenever documentation was available to support the practice, the methods were written to incorporate a high-resolution analytical technique—fused-silica capillary gas chromatography—and a highly specific detection technique—mass spectrometry. Also, whenever possible, high-performance liquid chromatography (HPLC) was recommended for the determination of compounds that could not be determined by gas chromatography with mass spectrometric detection (GC/MS). Nevertheless, there were many compounds for which limited documentation was available to support the recommendation of the use of either GC/MS or HPLC. Consequently, on the basis of the demonstrated need to reduce the number and complexity of analytical methods in the Methods Manual, we developed generalized GC/MS and HPLC techniques for the determination of as many as possible of the chemicals on the list of hazardous wastes. In the effort described in the subsequent sections of this manuscript, we concentrated on about 70 POHCs.

TECHNICAL APPROACH

General Considerations

The focus of our experimental work was to develop two generalized analytical methods for the determination of POHCs in appropriate organic solvents. One analytical technique involved GC/MS with the use of a capillary column, and the other involved HPLC with reverse-phase C_{18} columns and with ultraviolet spectrophotometric detection (HPLC/UV). During the optimization of the GC methods, flame ionization detection (FID)—in addition to MS—was employed to aid in establishing operating conditions.

We gave no consideration to the modification of sampling procedures or sample-preparation procedures reported in the Methods Manual. Changes in these procedures were beyond the scope of the present assignment. The investigation described here involved the development of instrumental analytical methods using solutions of the selected POHCs in solvents that were compatible with GC/MS or HPLC/UV determinations.

The laboratory work was structured to lead systematically from the determination of the feasibility of developing generalized test methods to the calibration of the ensuing methods for selected POHCs. First, we selected (largely on the basis of commercial availability) a variety of POHCs (from Appendix VIII, Part 261, 40 CFR) for preliminary investigation. Included in this selection were a variety of compound types including alcohols, esters, chlorinated aliphatics and aromatics, carboxylic acids and acid anhydrides, aliphatic and aromatic amines, nitrated aromatics, nitrosamines, hydrazines, nitriles, organosulfur compounds, and polynuclear aromatics and heterocyclics. We then analyzed standard solutions of mixtures of these POHCs (in appropriate solvents) to optimize instrumental operating conditions. Once suitable operating conditions had been established, we analyzed a series of standard solutions of each of the selected POHCs to estimate detection limits and to establish calibration curves.

GC Analysis Procedures

Description of instruments and general operating conditions. We developed the GC/MS generalized test method on the Hewlett-Packard Model 5985 Gas Chromatograph-Mass Spectrometer-Data System. The supplemental GC/FID work was performed with a Hewlett-Packard Model 5840 Gas Chromatograph that was equipped for use with capillary columns.

The work with both GC/MS and GC/FID involved capillary chromatography with matched, fused-silica SE-54 wall-coated capillary columns. The initial operating conditions were chosen as a compromise of the conditions given for several capillary GC methods in the Methods Manual. The initial starting column temperature was 40 °C; the temperature was then programmed at 10 °C/min to 280 °C and maintained at 280 °C for 15 min. The carrier gas, helium, was maintained at a volume flow rate through the column of about 2 mL/min. In the GC/FID work, the carrier gas flow was split downstream from the injection port in the conventional manner at a ratio of about 1 part to the column for every 40 parts vented. Thus, only a few percent of an injected sample was actually passed onto the column. In the GC/MS work, the "splitless" injection technique was employed. Consequently, we assumed that essentially all of the injected sample reached the column in GC/MS determinations.

Optimization and calibration of GC/FID procedure. GC operating conditions were optimized by analyzing methylene chloride solutions containing a variety of the candidate POHCs by the GC/FID technique. The column head pressure was adjusted to maximize the FID response to test mixtures. We used these adjustments to pinpoint the optimum carrier gas velocity, which in turn defined the splitting ratio.

Once we had established the optimum operating conditions, we calibrated the GC/FID procedure with external standards and prepared a five-point calibration curve for each of the POHCs investigated by GC. Each curve was a plot of the FID response (in peak area counts) as a function of the quantity of the particular POHC on the GC column. The detection limit for each candidate POHC was estimated as the quantity of the POHC on the GC column that gave rise to a signal approximately twice the background noise level.

Optimization and calibration of GC/MS procedure. Having established GC operating conditions by the GC/FID procedure, we then applied the method to the determination of the candidate POHCs by GC/MS. We also established reference mass spectra for the identification of the individual POHCs. The mass spectrometer was operated in a full-mass-scanning range (41 to 350 or 450 amu) in the electron impact (EI) mode. The scan time was maintained at ≤ 1 s to enable the collection of enough scans to characterize each capillary GC peak. To ensure the agreement of our work with that of others, we tuned the instrument to meet the spectral criteria for decafluorotriphenylphosphine according to the requirements given in EPA Method No. 625 (3).

As in the GC/FID work, standard solutions of the candidate POHCs in methylene chloride were used to calibrate the GC/MS technique. A five-point calibration curve was prepared for each compound by plotting the ion current for a selected mass fragment as a function of the injected quantity of the compound.

GC quality control procedures. In addition to the use of external standards for the calibration of both the GC/FID and GC/MS methods and in addition to the use of decafluorotriphenylphosphine for tuning the mass spectrometer, other quality control measures were also implemented. The precision of determinations by GC/FID and GC/MS was assessed by triplicate injections of at least one standard solution of each POHC investigated by GC. Furthermore, an internal standard, d_{10}-anthracene, was injected along with the analytes to minimize the effect of injection volume and instrument performance upon the precision of determinations.

HPLC Analysis Procedures

For the development of a generalized HPLC analysis procedure, we used the Hewlett-Packard Model 1084B High-Performance Liquid Chromatograph equipped with a variable wavelength UV detector (range of 190 to 600 nm) and an automatic sampling system. The following reverse-phase columns were used with an acetonitrile/water eluent:

- Perkin-Elmer HC-ODS-Sil-X-1, 10-μm particle size, 25-cm-long, 2.6-mm-i.d.
- Waters Associates μBondapak C_{18}, 10-μm particle size, 30-cm-long, 3.9-mm-i.d.

The Waters column was employed only after we found that a few of the candidate POHCs either were not retained by the Perkin-Elmer column or did not chromatograph well on the Perkin-Elmer column.

Rather than attempt to establish one rigid set of HPLC operating conditions for the method, our strategy in the development of a generalized HPLC method was to identify various procedural options that would allow determinations of a broad range of compound types. Consequently, we investigated the use of numerous isocratic and gradient elution programs with the acetonitrile/water mobile phase. In the determination of several POHCs (including the phenoxyacetic acid), the eluent was acidified. The wavelength of UV detection was also varied as required to optimize sensitivity. A Cary Model 17 Spectrophotometer was used to establish an absorption maximum in the range of 190 to 600 nm that would be suitable for the quantification of each POHC by the UV detector of the HPLC instrument.

As in the GC investigations, we determined the precision of the method with replicate injections of standard solutions of the analytes; however, an internal standard was not used in these determinations. The precision of analysis was determined for only a representative group of the compounds investigated by HPLC.

RESULTS AND DISCUSSION

GC Analysis

Table 1 presents the GC/FID results. The retention time and on-column detection limit are given for each compound. The compounds are listed in the order of their elution from the GC column. Retention times are relative to that observed for the internal standard, d_{10}-anthracene. The on-column detection limit is the quantity of each analyte that was estimated to yield an FID response of twice the background noise; three-fourths of the detection limits were in the subnanogram range.

A chromatogram of a mixture of all of the candidate POHCs investigated by GC/FID is presented in Figure 1. The chromatogram demonstrates the observed absolute retention times, the peak shapes, and any shifts in the base line that occurred. Although two of the candidate POHCs may not coexist in a field situation and therefore may not require simultaneous determination, the chromatogram demonstrates the resolving power of the capillary column.

Each reference calibration curve was a point-to-point plot of FID response as a function of the quantity of the analyte on the GC column, which was calculated from the quantity injected and the split ratio. Each plot can be used to estimate the sensitivity expected in the determination of a particular analyte. In generating these curves, we made no attempt to determine the upper limit of the linear range of determinations; however, each plot demonstrated the linearity of response within the range of quantities investigated. Linear regression analysis of the curves typically yielded correlation coefficients of ≥ 0.999. A typical curve (the curve for *N*-nitrosopyrrolidine) is presented as Figure 2.

Table 2 summarizes the GC/MS determinations. As in Table 1, the retention times are given relative to the internal standard, d_{10}-anthracene. Table 2 also lists the five most abundant mass fragments of each compound and, moreover, specifies the mass of the ion of each compound that was used for the establishment of detection limits and for the generation of calibration curves. The detection limits are the quantities of the analytes that were estimated to yield ion currents (of the selected ions) corresponding to about twice the background ion currents. Typical values of the detection limits were 1 to 5 ng.

Reference ion chromatograms, calibration curves, and mass spectra were generated for each of the compounds listed in Table 2. A chromatogram for the determination of a mixture of all of the compounds investigated by GC/MS is presented in Figure 3.

Several compounds were determined by GC/FID but were not determined by GC/MS. These compounds—methylhydrazine, dimethylhydrazine, and ethylenediamine—were volatile enough to be partially swept from the splitless injector of the GC/MS

TABLE 1. SUMMARY OF GC/FID DETERMINATIONS OF CANDIDATE POHCs

Compound	Relative retention time,[a] min	On-column detection limit,[b] ng
Methylhydrazine	0.06	0.45
1,2-Dimethylhydrazine	0.07	3.8
Ethylenediamine	0.08	0.43
N-Nitroso-*N*-methylethylamine	0.18	0.58
Malononitrile	0.20	0.62
Dimethyl sulfate	0.21	4.9
1,3-Dichloro-2-propanol	0.23	0.60
N-Nitrosodiethylamine	0.24	0.18
N-Nitroso-*N*-methylurethane	0.27	2.2
Ethyl methanesulfonate	0.28	0.70
Pentachloroethane	0.30	1.1
Benzyl chloride	0.34	0.20
N-Nitrosopyrrolidine	0.41	0.22
2,6-Dichlorophenol	0.53	1.5
4-Chloroaniline	0.53	0.20
N-Nitrosodibutylamine	0.59	0.21
Safrole	0.61	0.26
3,4-Diaminotoluene	0.63	0.39
1,2,4,5-Tetrachlorobenzene	0.64	0.49
Nicotine	0.66	0.35
2,4,5-Trichlorophenol	0.67	1.7
2,6-Diaminotoluene	0.70	0.11
2,4-Diaminotoluene	0.70	1.7
1,4-Naphthoquinone	0.72	0.44
p-Dinitrobenzene	0.73	0.53
m-Dinitrobenzene	0.75	0.12
Pentachlorobenzene	0.81	0.67
α-Naphthylamine	0.82	0.23
p-Nitroaniline	0.88	0.48
2-Acetamidofluorene	1.38	0.37
9,10-Dimethyl-1,2-benzanthracene	1.60	1.4
Dibenz[a,j]acridine	1.93	0.82

[a] Relative to the retention time of d_{10}-anthracene, 16 min.

[b] Quantity required to yield a response twice the magnitude of the background signal.

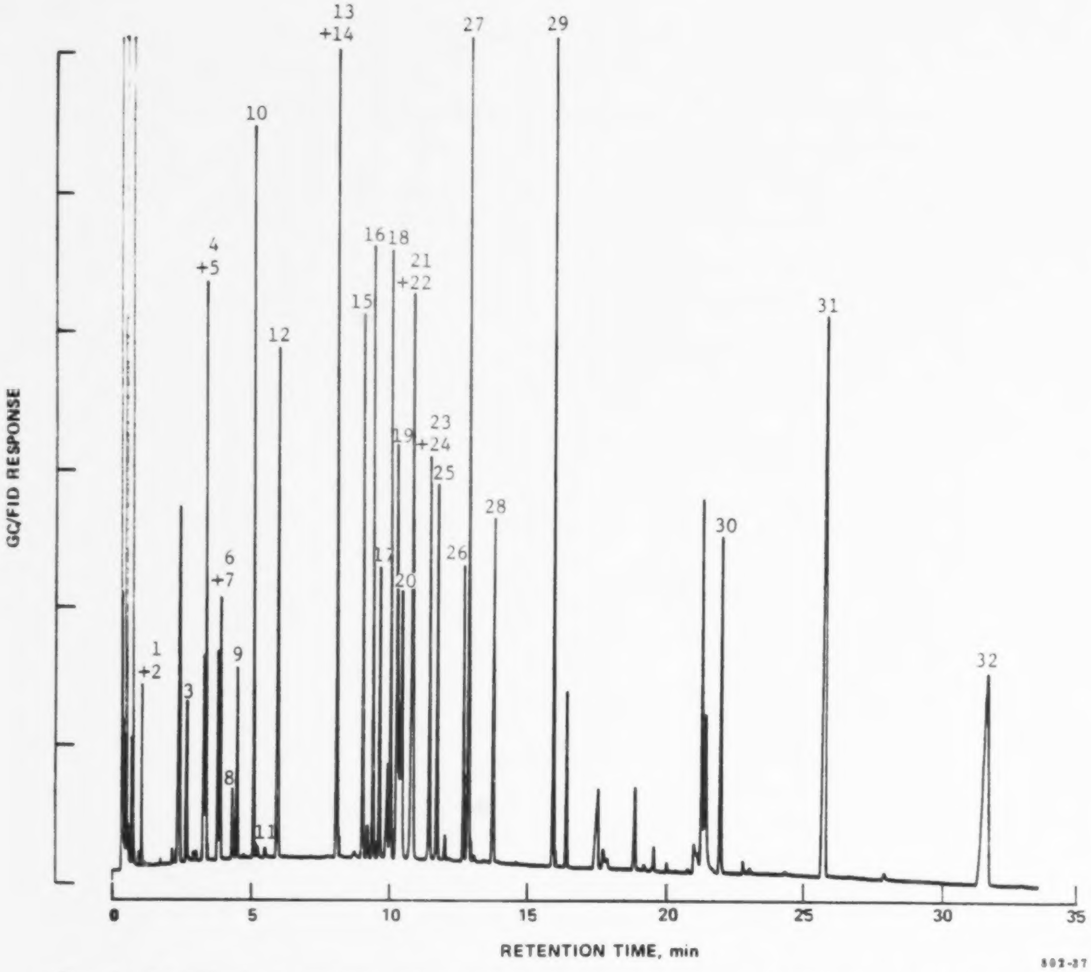

Figure 1. Chromatogram of all candidate POHCs by GC/FID. Peak 1: methylhydrazine; 2: 1,2-dimethylhydrazine; 3: N-nitroso-N-methylethylamine; 4: malononitrile; 5: dimethyl sulfate; 6: 1,3-dichloro-2-propanol; 7: N-nitrosodiethylamine; 8: N-nitroso-N-methylurethane; 9: ethyl methanesulfonate; 10: pentachloroethane; 11: benzyl chloride; 12: N-nitrosopyrrolidine; 13: 2,6-dichlorophenol; 14: 4-chloroaniline; 15: N-nitrosodibutylamine; 16: safrole; 17: 3,4-diaminotoluene; 18: 1,2,4,5-tetrachlorobenzene; 19: nicotine; 20: 2,4,5-trichlorophenol; 21: 2,6-diaminotoluene; 22: 2,4-diaminotoluene; 23: 1,4-naphthoquinone; 24: p-dinitrobenzene; 25: m-dinitrobenzene; 26: pentachlorobenzene; 27: α-naphthylamine; 28: p-nitroaniline; 29: d_{10}-anthracene; 30: 2-acetamidofluorene; 31: 9,10-dimethyl-1,2-benzanthracene; 32: dibenz[a,j]acridine.

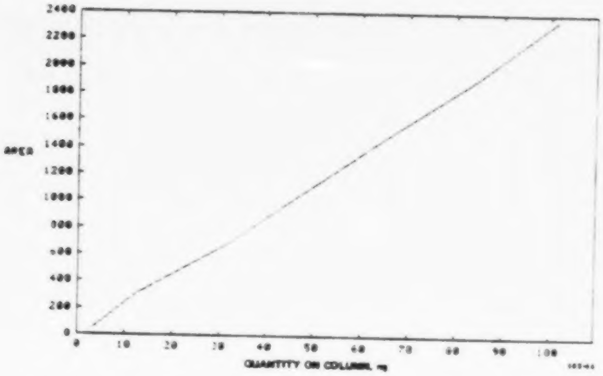

Figure 2. Calibration curve for N-nitrosopyrrolidine by GC/MS.

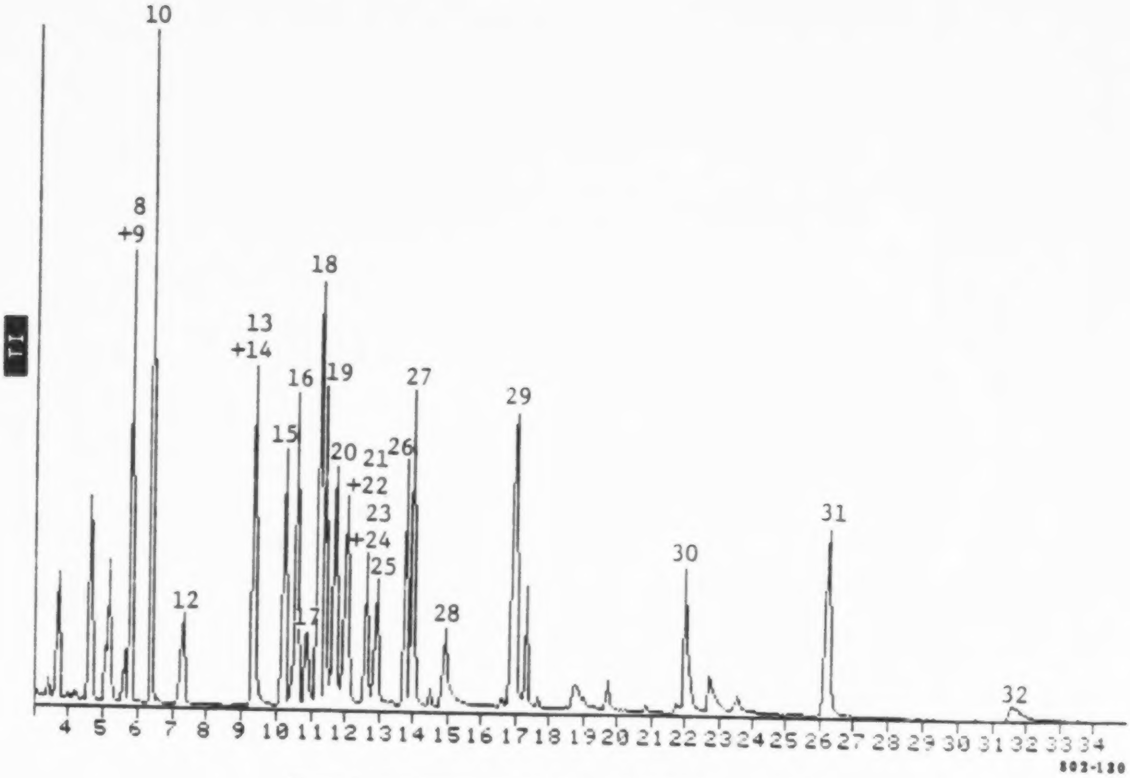

Figure 3. Chromatogram of all candidate POHCs by GC/MS.

TABLE 2. SUMMARY OF GC/MS DETERMINATIONS OF CANDIDATE POHCs

Compound	Relative retention time,[a] min	On-column detection limit,[b] ng	Mol wt	Masses of characteristic EI ions (relative abundance) 1[c]	2	3	4	5
N-Nitroso-N-methylethylamine	0.21	4.8	88	88(100)	42(93)	43(46)	56(24)	71(13)
Malononitrile	0.24	5.6	66	66(100)	65(12)	64(9)	67(5)	50(5)
Dimethyl sulfate	0.24	4.0	126	95(100)	96(76)	66(28)	79(20)	65(16)
1,3-Dichloro-2-propanol	0.26	6.1	129	79(100)	81(38)	43(27)	49(20)	42(8)
N-Nitrosodiethylamine	0.27	2.7	102	102(100)	42(68)	44(60)	56(56)	57(36)
N-Nitroso-N-methylurethane	0.29	23	132	43(100)	96(76)	66(28)	79(20)	65(10)
Ethyl methanesulfonate	0.30	5.2	124	79(100)	109(78)	97(26)	80(19)	65(14)
Pentachloroethane	0.34	1.2	202	117(100)	119(87)	167(82)	165(65)	169(41)
Benzyl chloride	0.37	0.7	126	91(100)	126(16)	65(16)	63(11)	89(9)
N-Nitrosopyrrolidine	0.43	1.9	100	100(100)	41(61)	42(58)	68(16)	43(14)
2,6-Dichlorophenol	0.55	1.7	163	162(100)	164(62)	63(58)	98(34)	99(15)
4-Chloroaniline	0.55	1.9	128	127(100)	65(51)	129(38)	92(29)	100(30)
N-Nitrosodibutylamine	0.60	4.8	154	84(100)	57(73)	41(61)	42(40)	99(25)
Safrole	0.62	0.09	162	162(100)	104(78)	77(62)	131(60)	135(36)
3,4-Diaminotoluene	0.64	10	122	122(100)	121(71)	94(42)	77(22)	106(21)
1,2,4,5-Tetrachlorobenzene	0.66	1.3	216	216(100)	214(85)	218(52)	74(37)	181(24)
Nicotine	0.67	4.2	162	84(100)	133(38)	42(21)	162(19)	161(18)
2,4,5-Trichlorophenol	0.70	2.2	197	198(100)	196(96)	97(58)	200(31)	132(29)
2,6-Diaminotoluene	0.71	2.4	122	122(100)	121(63)	104(36)	94(33)	106(20)
2,4-Diaminotoluene	0.71	10	122	121(100)	122(90)	94(29)	77(19)	105(16)
1,4-Naphthoquinone	0.73	3.6	158	158(100)	102(67)	104(66)	76(62)	130(45)
p-Dinitrobenzene	0.74	1.5	168	168(100)	76(82)	50(80)	75(78)	122(34)
m-Dinitrobenzene	0.76	1.5	168	168(100)	76(92)	50(82)	75(75)	122(32)
Pentachlorobenzene	0.81	1.0	250	250(100)	252(62)	248(62)	108(41)	54(21)
α-Naphthylamine	0.82	0.4	143	143(100)	115(51)	116(29)	144(12)	89(11)
p-Nitroaniline	0.88	5.1	138	138(100)	65(85)	108(74)	92(40)	80(24)
2-Acetamidofluorene	1.34	3.7	223	181(100)	180(82)	223(62)	152(37)	153(19)
9,10-Dimethyl-1,2-benzanthracene	1.54	4.9	256	256(100)	241(54)	239(36)	240(36)	257(19)
Dibenz[a,j]acridine	1.88	12	279	279(100)	280(38)	277(19)	125(14)	139(11)

[a] Relative to the retention time of d_{10}-anthracene, 16 min.

[b] Quantity required to yield a response twice the magnitude of the background signal.

[c] This ion was used for quantification.

system along with the solvent and thus were not determined. It is likely that these compounds could be determined, with some loss in sensitivity, by GC/MS with split injection techniques.

Some other compounds investigated could not be determined reliably by GC/FID or GC/MS. These included maleic anhydride, thiophenol, cyclophosphamide, and o-toluidine. Apparently these compounds either were irreversibly sorbed by the GC column or were decomposed in solution, on the column, or in the injection port.

Table 3 presents the results of triplicate GC/FID determinations of approximately 0.05-µg quantities of all of the candidate POHCs listed in Table 1 except the hydrazines. The calculated values of the standard deviation (SD) and relative standard deviation (RSD) in Table 3 indicate that most GC/FID determinations were very precise. RSDs greater than about 5% were, however, obtained for several of the compounds—N-nitrosodiethylamine, N-nitroso-N-methylurethane, ethyl methanesulfonate, pentachloroethane, benzyl chloride, 2,6-dichlorophenol, and 1,2,4,5-tetrachlorobenzene. The less precise determinations were the result of anomalously low responses obtained with the first in the series of three determinations for each of these compounds. Perhaps at least one injection was required to condition the GC column and thereby to prevent loss of the compounds in subsequent injections.

Table 4 presents the results of triplicate GC/MS determinations of about 0.1-µg quantities of all of the POHCs listed in Table 2 except malononitrile. In general, the GC/MS determinations were less precise than the GC/FID determinations. Nevertheless, about two-thirds of the compounds were determined with an RSD of <5%. Several of the compounds for which we obtained relatively imprecise determinations by GC/FID were also found to yield RSDs of >5% by GC/MS; these included N-nitrosodiethylamine, pentachloroethane, and benzyl chloride.

HPLC Analysis

Six procedural options were included in the generalized HPLC/UV method. Three were formulated for the Perkin-Elmer reverse-phase C_{18} column; three for the Waters column. The options for both columns were either variations of the isocratic composition of the acetonitrile/water mobile phase or variations of the solvent program. The various procedures for the Perkin-Elmer column were as follows:

- Option 1A

Solvent A: Distilled, deionized water
Solvent B: Acetonitrile
Solvent program: 10% B, 5 min; 10 to 100% B in 35 min; 100% B, 10 min
Solvent flow rate: 1 mL/min

- Option 1B

Solvent A: 1% (v/v) acetic acid in distilled, deionized water
Solvent B: Acetonitrile
Solvent program: 20% B, 10 min; 20 to 50% B in 10 min; 50% B, 5 min
Solvent flow rate: 2 mL/min

- Option 1C

Solvent A: 1% (v/v) acetic acid in distilled, deionized water
Solvent B: Acetonitrile
Solvent program: 10% B, 2 min; 10 to 100% B in 18 min
Solvent flow rate: 2 mL/min

The various procedures for the Waters column were as follows:

- Option 2A

Solvent A: Distilled, deionized water
Solvent B: Acetonitrile
Solvent program: 2% B, isocratic
Solvent flow rate: 1 mL/min

TABLE 3. PRECISION OF GC/FID DETERMINATIONS

Compound	Relative GC/FID response[a]					
	Detn[b] No. 1	Detn No. 2	Detn No. 3	Mean	SD	RSD, %
Ethylenediamine	19.2	19.6	18.5	19.1	0.6	2.9
N-Nitroso-*N*-methylethylamine	1.70	1.75	1.61	1.69	0.07	4.2
Malononitrile	8.34	9.12	8.72	8.73	0.39	4.5
Dimethyl sulfate	16.4	16.3	15.3	16.0	0.6	3.9
1,3-Dichloro-2-propanol	3.44	3.76	3.79	3.66	0.19	5.3
N-Nitrosodiethylamine	1.24	1.45	1.27	1.32	0.11	8.5
N-Nitroso-*N*-methylurethane	5.66	6.16	6.41	6.08	0.38	6.3
Ethyl methanesulfonate	3.12	3.81	3.62	3.52	0.36	10.2
Pentachloroethane	3.94	4.47	4.41	4.27	0.29	6.9
Benzyl chloride	1.00	1.12	1.12	1.08	0.07	6.5
N-Nitrosopyrrolidine	1.06	1.15	1.07	1.09	0.05	4.4
2,6-Dichlorophenol	2.11	2.30	2.40	2.27	0.14	6.4
4-Chloroaniline	1.23	1.32	1.23	1.26	0.05	4.2
N-Nitrosodibutylamine	1.09	1.17	1.11	1.12	0.04	4.0
Safrole	1.32	1.35	1.38	1.35	0.03	2.0
3,4-Diaminotoluene	1.06	1.07	1.04	1.06	0.02	1.7
1,2,4,5-Tetrachlorobenzene	2.11	2.39	2.39	2.30	0.16	7.0
Nicotine	1.35	1.38	1.36	1.36	0.02	1.1
2,4,5-Trichlorophenol	2.24	2.29	2.23	2.25	0.03	1.3
2,6-Diaminotoluene	1.27	1.27	1.28	1.27	0.01	0.6
2,4-Diaminotoluene	1.07	1.04	1.06	1.06	0.01	1.2
1,4-Naphthoquinone	2.47	2.61	2.33	2.47	0.14	5.6
p-Dinitrobenzene	2.29	2.29	2.28	2.29	0.002	0.1
m-Dinitrobenzene	1.86	1.84	1.83	1.84	0.01	0.7
Pentachlorobenzene	2.41	2.66	2.67	2.58	0.15	5.7
α-Naphthylamine	0.86	0.88	0.89	0.88	0.02	1.9
p-Nitroaniline	1.31	1.27	1.28	1.29	0.02	1.6
2-Acetamidofluorene	1.43	1.44	1.48	1.45	0.02	1.7
9,10-Dimethyl-1,2-benzanthracene	0.927	0.927	0.920	0.924	0.004	0.4
Dibenz[a,j]acridine	1.37	1.35	1.36	1.36	0.01	0.8

[a] (Peak area of internal standard)/(Peak area of POHC).

[b] Detn = determination.

TABLE 4. PRECISION OF GC/MS DETERMINATIONS

Compound	Relative GC/MS response[a]					
	Detn[b] No. 1	Detn No. 2	Detn No. 3	Mean	SD	RSD, %
N-Nitroso-*N*-methylethylamine	7.39	7.71	7.47	7.52	0.17	2.2
Dimethyl sulfate	4.31	4.60	4.08	4.33	0.26	6.0
1,3-Dichloro-2-propanol	4.76	4.79	4.41	4.65	0.21	4.5
N-Nitrosodiethylamine	3.66	3.45	4.01	3.71	0.28	7.6
N-Nitroso-*N*-methylurethane	7.45	7.56	7.00	7.34	0.29	4.0
Ethyl methanesulfonate	3.18	3.14	2.97	3.10	0.11	3.6
Pentachloroethane	6.19	5.33	5.27	5.60	0.51	9.2
Benzyl chloride	1.43	1.77	1.77	1.66	0.20	11.8
N-Nitrosopyrrolidine	3.04	3.35	3.60	3.33	0.28	8.4
2,6-Dichlorophenol	3.51	3.64	3.42	3.52	0.11	3.2
4-Chloroaniline	1.98	1.87	1.95	1.93	0.06	3.1
N-Nitrosodibutylamine	2.58	2.92	3.11	2.87	0.27	9.2
Safrole	4.91	5.08	5.12	5.04	0.11	2.2
3,4-Diaminotoluene	5.12	5.32	5.49	5.31	0.19	3.5
1,2,4,5-Tetrachlorobenzene	3.81	3.68	3.44	3.64	0.19	5.1
Nicotine	2.47	2.87	2.40	2.58	0.25	9.8
2,4,5-Trichlorophenol	2.62	2.54	2.44	2.54	0.10	3.6
2,6-Diaminotoluene	4.70	4.80	4.81	4.77	0.06	1.3
2,4-Diaminotoluene	2.50	2.50	2.58	2.52	0.05	1.8
1,4-Naphthoquinone	2.59	2.77	2.68	2.68	0.09	3.3
p-Dinitrobenzene	11.8	12.0	12.2	12.0	0.2	1.4
m-Dinitrobenzene	5.36	4.82	5.08	5.09	0.27	5.2
Pentachlorobenzene	3.81	4.03	3.96	3.93	0.11	2.9
α-Naphthylamine	1.14	1.12	1.16	1.14	0.02	1.6
p-Nitroaniline	6.51	5.76	6.02	6.10	0.38	6.2
2-Acetamidofluorene	4.81	5.59	5.39	5.26	0.40	7.7
9,10-Dimethyl-1,2-benzanthracene	23.4	24.6	32.2	26.7	4.8	17.9
Dibenz[a,j]acridine	3.12	3.35	3.75	3.41	0.32	9.2

[a] (Peak area of internal standard)/(Peak area of POHC).

[b] Detn = determination.

- Option 2B

  Solvent A: Distilled, deionized water
  Solvent B: Acetonitrile
  Solvent program: 10% B, isocratic
  Solvent flow rate: 1 mL/min

- Option 2C

  Solvent A: Distilled, deionized water
  Solvent B: Acetonitrile
  Solvent program: 20% to 100% B in 20 min; 100% B, 10 min
  Solvent flow rate: 1 mL/min

In Table 5, the option used in the determination of each compound investigated by HPLC/UV is specified. Two-thirds of the listed compounds were determined by Option 1A. Option 1B, which involved the acidification of the eluent, was instituted primarily for the determination of the phenoxyacetic acids. We observed that 4,6-dinitro-o-cresol and methyl yellow chromatographed very poorly without the inclusion of acid in the eluent; thus, Option 1C was established for the determination of these two compounds. Option 2A was suitable for the determination of N-nitroso-N-methylurea; Option 2B for saccharin. (Option 2C was used for the determination of other compounds discussed later. See Table 6.) For some of the compounds, it is likely that another option—either one of the other options listed here or a new set of operating conditions—would have given results comparable to those presented in Table 5.

The application of the specified procedures yielded the retention times and detection limits given in Table 5. For most of the compounds listed, the initial determinations were made at a detector wavelength of 254 nm, the wavelength of maximum absorbance for the phenyl functional group. After we had selected optimum wavelengths for analysis, we redetermined some of the compounds to establish lower detection limits. The limits established for the optimum wavelengths were typically <10 ng and usually at least a factor of 10 lower than the limits at 254 nm.

Reference chromatograms, UV spectra, and calibration curves were generated for the compounds listed in Table 5. The calibration curves typically yielded linear-least-squares correlation coefficients of ≥ 0.999. For some exceptions, such as phenol, we obtained calibration curves that were nonlinear. Because these curves did appear to be useful in determining the substances with reasonable accuracy, however, we did not consider it necessary to determine these substances on other HPLC columns or with alternative solvent programs.

In addition to the compounds cited in Table 5, we found others that may be determined by the generalized HPLC/UV test procedure. Because of time constraints, the investigation of these substances was not completed; nevertheless, several compounds are presented in Table 6 as potential candidates for analysis by the HPLC procedure. Retention times and approximate detection limits were determined for the compounds on the basis of a limited number of injections of standard solutions. The retention times of several of the compounds—thiourea, thioacetamide, and ethylene thiourea—were uncertain because several major peaks were observed in their chromatograms. The presence of more than one major peak in a chromatogram was interpreted as an indication of gross contamination of the sample or as an indication of the decomposition of the analyte on the HPLC column. Thus, the feasibility of the application of the method to the determination of these four compounds is uncertain.

The precision of HPLC determinations for a representative group of the candidate POHCs is demonstrated by the data in Table 7. All but two of the triplicate sets of results were very precise. The precision of the determinations of acetophenetidin was biased by one value that was 15% higher than the other two. Perhaps additional replicate determinations would have proven the high result to be a statistical outlier. The determinations of 5-nitro-o-toluidine yielded increasing responses with each subsequent determination; such a trend is usually indicative of column conditioning. Perhaps the response would have reached a stable value after repeated injections.

TABLE 5. SUMMARY OF HPLC/UV DETERMINATIONS OF CANDIDATE POHCs

Compound	Procedural option[a]	Retention time, min	On-column detection limit,[b] ng	Wavelength of detection, nm
Streptozotocin	1A	1.4	2	254
			--	230[c]
Phenol	1A	5.4	78	254
			--	280[c]
4-Nitrophenol	1A	9.5	54	254
			6	280[c]
o-Chlorophenol	1A	12.4	72	254
			6	280[c]
Acetophenetidin	1A	12.6	1	254
			--	248[c]
5-Nitro-*o*-toluidine	1A	14.3	1	254
			--	253[c]
Tetramethylthiouram disulfide	1A	16.3	1	254
			--	280[c]
4-Chloro-*m*-cresol	1A	16.8	77	254
			4	280[c]
2,4-Dichlorophenol	1A	17.6	100	254
			2	280[c]
3-(α-Acetonylbenzyl)-4-hydroxycoumarin	1A	19.8	2	254
			--	280[c]
2,4,6-Trichlorophenol	1A	20.0	53	254
			7	280[c]
2,3,4,6-Tetrachlorophenol	1A	21.5	19	254
			17	280[c]
Reserpine	1A	22.7	28	254
			--	267[c]
Chlorambucil	1A	23.9	1	254
			--	258[c]
2,4-Dichlorophenoxyacetic acid	1B	7.6	69	254
			--	284[c]
2,4,5-Trichlorophenoxyacetic acid	1B	14.2	55	254
			--	287[c]
2-(2,4,5-Trichlorophenoxy)-propionic acid	1B	16.5	38	254
			--	287[c]
4,6-Dinitro-*o*-cresol	1C	7.6	20	378[c]
Methyl yellow	1C	13.1	3	400[c]
N-Nitroso-*N*-methylurea	2A	8.4	10	254
			--	234[c]
Saccharin	2B	3.2	2	254
			--	224[c]

[a] See text for description of options.

[b] Quantity injected that is required to yield a response twice the magnitude of background signal.

[c] This wavelength was selected from the referenced UV spectrum as the optimum wavelength for analysis.

TABLE 6. POTENTIAL CANDIDATES FOR ANALYSIS BY HPLC/UV

Compound	Procedural option[a]	Retention time, min	Approximate on-column detection limit,[b] ng	Wavelength of detection, nm
Trypan blue	2C	3	20	315
Epinephrine	2C	3	60	279
Thiosemicarbazide	2C	3	5	254
Thiourea	2C	~3[c]	6	254
Thioacetamide	2C	~4[c]	2	254
Ethylene thiourea	2C	~4[c]	8	254
Crotonaldehyde	2C	5	1	230
Diethylstilbestrol	2C	14	4	240
Mitomycin C	1A	5	17	254
Melphalan	1A	14	10	254
3,3'-Dimethoxybenzidine dihydrochloride	1A	~19	9	254
Daunomycin	1B	8	75	254
Azaserine	2A	4	2	254

[a] See text for description of options.

[b] Quantity injected that should yield a response of 1000 counts on the integrator.

[c] The presence of several major peaks in the chromatogram made the assignment of a retention time difficult.

TABLE 7. PRECISION OF HPLC DETERMINATIONS

Compound	Quantity injected, μg	HPLC/UV response, area counts x 10^{-3}			Mean	SD	RSD, %
		Detn[a] No. 1	Detn No. 2	Detn No. 3			
3-(α-Acetonylbenzyl)-4-hydroxycoumarin	9.39	895	886	902	894	8	0.9
Acetophenetidin	2.52	1060	915	909	962	85	8.9
Chlorambucil	1.76	452	449	457	452	4	0.9
N-Nitroso-*N*-methylurea	4.96	109	108	107	108	1	0.8
5-Nitro-*o*-toluidine	2.48	690	750	801	747	56	7.4
Reserpine	7.50	58.4	56.4	61.4	58.8	2.5	4.2
Saccharin	0.98	43.0	43.2	42.0	42.7	0.7	1.5
Tetramethylthiuram disulfide	9.45	264	266	264	264	1	0.4

[a] Detn = determination.

SUMMARY AND CONCLUSIONS

A generalized GC/MS (and GC/FID) test procedure and a generalized HPLC/UV procedure have been developed for the determination of approximately 70 candidate POHCs. Additional details of the methods evaluation and reference chromatograms, calibration curves, mass spectra, and UV spectra are given in Reference 2.

The candidate POHCs are of a variety of compound types including alcohols, esters, chlorinated aliphatics and aromatics, carboxylic acids and acid anhydrides, aliphatic and aromatic amines, nitrated aromatics, nitrosamines, hydrazines, nitriles, organosulfur compounds, and polynuclear aromatics and heterocyclics. The generalized procedures are likely to be applicable to the determination of compounds similar to those tested.

The methods have been calibrated for candidate POHCs over concentration ranges of interest and have demonstrated acceptable precision in the determination of most of the POHCs. The ultimate accuracy of the methods in the determination of POHCs in incinerator wastes and effluent will, of course, depend on the prudent choice of appropriate sampling procedures and sample-preparation procedures.

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NEW IDEAS IN HAZARDOUS WASTE MANAGEMENT TECHNOLOGY

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ABSTRACT

This paper discusses the initial results of an EPA/State of California co-sponsored project to evaluate emerging innovative technologies for managing hazardous wastes. Over 40 proposals submitted by various waste management technology developers were evaluated by an Office of Appropriate Technology (OAT) technical panel to select 12 for possible demonstration within California. The selected proposals, which include five thermal, two biological and five physical/chemical processes, are briefly discussed.

INTRODUCTION

Under a cooperative agreement initiated in March 1980 with the U.S. EPA, the California Office of Appropriate Technology (OAT) has begun a project to evaluate and possibly demonstrate innovative processes for treating and detoxifying hazardous wastes. The project is part of a program supported by various State agencies to encourage the detoxification, reduction, recycling, or destruction of hazardous wastes as an alternative to landfills.

Processes for this project were obtained primarily from a request for proposals which was run in several prominent technical and environmental magazines. A review panel consisting of OAT staff members selected 12 processes from the approximately 45 submitted. The technologies chosen for further evaluation are shown in Table I. Discussion of the technologies follows. The inclusion of these processes in this paper is not intended to be an endorsement of the processes by either OAT or EPA. Neither OAT nor EPA, at this time, have evaluated the claims made for the processes or in any way determined their accuracy. This is the purpose of the study which will follow. Persons interested in learning more about these technologies are urged to talk with the contact person indicated.

THERMAL PROCESSES

Pyrolytic Incineration
Midland Ross Corporation

The system as described by the vendor includes three components in sequence: a rotary hearth furnace, a rich fume reactor, and a heat recovery device. Waste is fed onto the rotary hearth and held at 1000° to 1400°F for 15 to 30 minutes depending upon the type of waste. As the waste is volatilized, the gaseous fraction is passed to the reactor and is combusted to complete the destruction of hazardous compounds. The reactor is reported to operate at temperatures in the range of 1800° to 3000°F depending upon the toxicity of gaseous components. Following combustion in the reactor, the gaseous fraction is released to a boiler for the extraction of heat energy.

The pyrolytic incineration process operates under quiescent atmosphere, so particulate carry over is claimed to be lower than for the conventional incineration process. Inorganic chemical constituents containing sulfur, phosphorus, and halides may be retained in the char because of lower pyrolysis temperature. Scrubbing equipment can be added, if need arises, to remove chemical pollutants such as SO_2, HCl, or P_2O_5 to meet emission standards. The process is commercially available.

Cement Kiln Co-Combustion
Systech Corporation

The process is to burn ignitable organic wastes as a supplemental fuel in a cement kiln at a location in Southern California. The project is patterned on a similar operation being run by the applicant at a plant in Ohio.

It is reported that at the Ohio plant, selected waste materials, waste solvents and industrial oils are procured directly from generators, transported to the facility using tank trucks, and off-loaded at the receiving station directly into the storage tanks located at the cement manufacturing facility. Chemical analyses are performed at the receiving station to assure that the materials received comply with the permit requirements, and to be sure that the materials delivered to the cement kiln comply with specifications designed to guarantee that the cement manufacturing process is not negatively impacted. The material is then pumped to the cement kiln and fired in conjunction with the standard fuel utilized in the kiln.

No environmental emissions are expected by the vendor from this process beyond the normal products from combustion processes. Particulate emissions, it is claimed, will remain consistent with those from the fossil fuels normally used in the cement kiln, and will be controlled by the existing air pollution control equipment on the kilns. All the organics are claimed to be completely destroyed in the kiln due to the high temperature and long retention times of the process. Metals or chlorine contained in the waste products are said to be incorporated in an essentially unleachable form into the cement product or the dust. The process may actually reduce the sulfur emission from the cement kilns due to the fact that less sulfur may be in the waste fuels than is present in the coal that is replaced (coal is used in 95% of the kilns in the United States).

High Temperature Fluid Wall
Thagard Research Company

The Thagard HTFW process is a high temperature process for quickly reducing organic wastes to their elemental state. The reduction is carried out in a patented reactor which consists of a tubular core of porous refractory material capable of emitting sufficient radiant energy to activate reactants fed into the tubular space. The core material is designed to be of uniform porosity to allow the permeation of a radiation-transparent gas through the core wall into the interior. The core is completely jacketed and insulated in a fluid-tight pressure vessel. Electrodes located in the annular space between jacket and core provide the energy required to heat the core to radiant temperatures.

The principle, it is claimed, which differentiates the HTFW Reactor from other high temperature devices is the method of energy transfer to the reactants. While the latter employs convective or conductive techniques to transfer energy to the Reactor feed, the HTFW Reactor, according to claims, uses radiative coupling to heat the reactants. The core is heated by the external electrodes and its inner surface re-radiates the energy into the tubular space where the reactants are introduced. Radiative power densities of over 1200 watts/in^2 are claimed, and the finely divided reactants are heated by the direct impingement of electromagnetic radiation. The advantages of this method of energy transfer are that the reactants are instantaneously heated, and the chemical reactions are greatly accelerated without the necessity for heating the entire process stream to reaction temperature. The rate of energy transfer is independent of either the contact of the reactants with the Reactor surfaces or of the flow regime of the reactants.

Another distinctive feature reported by the builder for the HTFW Reactor is the patented fluid-wall. A gas, which is transparent to the radiation (and therefore largely not energy consuming), is introduced radially through the porous walls of the Reactor to produce an annular envelope of gas which blankets the walls. This envelope reduces the contact of the reactants with the Reactor surfaces to minimize deposition of reactants or products on the radiator surface. This feature offers an improvement over other gasifiers, since the operational life of the Reactor components is not subject to slagging with its attendant core wear.

Because energy transfer is accomplished by radiation, heating of the reactants is claimed to be very rapid – on the order of millions of degrees per second for reactant surfaces. Normal operating temperatures are in the region of $4000^{\circ}F$. Externally published literature does not provide kinetic data and models for reactions at these temperatures, and most data derived by Thagard is at the state-of-the art. The vendor also claims evidence that in these temperature regimes, the reactions differ in kind, not simply in degree. However, empirical data from several thousand hours of Thagard testing shows that, in these ranges, the rate of surface heating tends to preclude the formation of intermediate compounds from partial reactions of feed material. Since these compounds may contribute to downstream pollution abatement requirements, their elimination would assure a higher level of product purity with reduced cost for downstream clean-up equipment. Reaction times are almost instantaneous. Residence time for reactants can be greatly reduced and reactor size can be minimized. Consequently, capital costs lower than systems based on lower-temperature processes are claimed.

Catalytic, Low Temperature Fluidized Bed
Energy Incorporated

The incineration process is described by the manufacturer as a catalytic, low temperature, fluidized bed process for the destruction of toxic and hazardous wastes. The system incorporates a dry exhaust gas clean-up method for removal of the process by-products.

As presented, liquid waste is metered (along with fuel oil when required) into an injection tube which pneumatically injects the waste near the bottom of a fluidized bed operating at a low temperature. The bed itself is composed of a mixture of granular combustion catalyst and limestone. Fluidizing air is forced up through this bed at a high enough velocity that the mixture behaves very similar to a boiling liquid. During operation, limestone is continuously added to the bed to replenish that expended by reaction with combustion products. Also during operation, bed material is periodically drained from the vessel to maintain the appropriate bed height.

In the pilot plant, a single cyclone separator is used to remove particulate matter from the off-gas. In a deliverable full sized system, it is likely that a multiclone or other more efficient particulate removal system would be necessary. During the past year, the EI fluidized bed incineration system has been demonstrated for the destruction of chlorinated hydrocarbons and organophosphates. The chlorinated waste demonstration has used carbon tetrachloride as a representative aliphatic hydrocarbon and dichlorobenzene as a representative aromatic hydrocarbon. Tributylphosphate has been used to represent organo phosphate materials. The program for further waste types to be evaluated includes phenols, chlorophenols, hexachlorobenzene, PCBs, and mixtures of these wastes. Optimization of fuel (where necessary), catalyst use, absorbent use, and system operating and design parameters are not complete so no complete process economics are now available. According to EI, preliminary data suggest that the technology may offer a considerable economic advantage over other systems because of low temperatures, reduced amount of fuel oil where required, and less exotic materials of construction.

Wet Air Oxidation
Zimpro, Inc.

Wet Air Oxidation is a process to oxidize dissolved or suspended organic substances at elevated temperatures and pressures. Water, which makes up the bulk of the aqueous phase, serves to catalyze the oxidation reactions so that they proceed at relatively low temperatures (350°F to 650°F) and at the same time serves to moderate the oxidation rates removing excess heat by evaporation. Water also provides a heat transfer medium which, it is claimed, enables the Wet Air Oxidation process to be thermally self-sustaining with relatively low organic feed concentrations. The process is believed by the vendor to be most useful for wastes too dilute to incinerate economically, yet too toxic to treat biologically.

The oxygen required by the Wet Air Oxidation reactions is provided by an oxygen-containing gas, usually air, bubbled through the liquid phase in a reactor used to contain the process; thus the commonly used term "wet air oxidation." The process pressure is maintained at a level high enough to prevent excessive evaporation of the liquid phase, generally between 300 and 3,000 psi.

As described by the manufacturer, a wastewater stream containing oxidizable contaminants is pumped to the system pressure by means of a positive displacement type pump. The wastewater passes through a heat exchanger which preheats the waste by indirect heat exchange with the hot oxidized effluent. The temperature of the incoming feed is increased to a level necessary to support the oxidation reaction in the reactor vessel. Air and the incoming liquid are injected into the reactor where the oxidation begins to take place. As oxidation progresses up through the reactor, the heat of combustion is liberated, increasing the temperature of the reaction mixture. This heat of oxidation is recovered by interchanging with the incoming feed thus giving, in many instances, thermally self-sustaining operation. After energy removal, the oxidized effluent, comprised mainly of water, carbon dioxide, and nitrogen is reduced in pressure through a specially designed automatic control valve, according to the manufacturer's designs.

BIOLOGICAL PROCESSES

Soil Enrichment
Veale Tract Farms

The applicant is an operating farm which applies various inorganic industrial by-products and wastes directly into the land to bring about soil enrichment. Much of the material handled by the process could be classified as hazardous wastes if it were to be disposed of in a commercial chemical landfill. Veale Tract Farms is not classified as a waste disposal site. All materials have been declassified as waste for use as agricultural soil amendment, after extensive analysis and review. All materials beneficial to agriculture are applied at recommended rates, and are used in an environmentally safe manner.

The applicant has conducted operations since 1975 and is currently the only such operation in the United States. Some of the materials utilized are limerock, paper pulp effluent, lime sulfur slurry, ammonium sulfate, digested sewage sludges, lime sludge, and gypsum.

There are no direct emissions from the operations. Indirectly, sodium and alkaline water is leached from the cropland and drained to a central location. The farm operates under discharge requirements set by the California Regional Water Quality Board. The operation appears to offer a very attractive alternative for at least some of the materials now going into landfills.

Specialized Microbes For
In Situ Hazardous Materials Control
Polybac Corporation

The process involves the addition of microbes specially developed to break down highly refractory toxic materials to conventional and specialized biological treatment processes. These microbes have been developed through a process of "selective adaptation" through increased exposure to model substrates, and subsequent mutation to genetically fix the biodegradation enhancement. The wastes for which this process can be used comprise a very broad list, ranging from dilute aqueous solutions through highly concentrated aqueous solutions, and including semi-solid and solid materials. Microbes have been developed for breaking down extremely refractory compounds such as 2,4-D and certain PCBs.

The biological process has been shown to be less energy intensive and expensive than other ultimate destruction technologies such as oxidation or incineration. The process also produces no secondary disposal problems for toxic residuals.

The end product of biodecontamination is carbon dioxide, water and cell mass. Where small quantities of waste are being degraded at a single site or where the decontamination is occurring in the soil, the final residue (the cell mass) is totally compatible with the natural bioprocess and will be readily reassimilated into the natural eco-system. Where very large amounts of wastes are being degraded at a single site, a substantial microbial residue will develop which must be handled. This residue can be handled through biological anaerobic digestion with the concomitant production of energy (methane gas). The final stable residue from anaerobic digestion can be ultimately used to re-establish the viability of lands which have been made sterile by man's activities. This would include stripped mine land reclamation, reforestation, etc.

PHYSICAL/CHEMICAL PROCESSES

Ultra Violet Disinfection
Pure Water Systems, Inc.

The process as reported uses ultra-violet light to accelerate the biological degradation of organic wastes in dilute concentrations. Although the mechanisms by which the UV process detoxifies chemicals is still under investigation, the reaction appears to be a chemical oxidation/reduction reaction involving the generation of ozone. Waste streams currently being studied are halogenated aromatic compounds, chlorodioxins, copper wastes, and waste streams from synthetic fuels production. The USDA pesticide laboratory has carried out research on the process and found that biological activity increased dramatically following pretreatment with UV. The USDA has entered into an agreement with the appplicant to construct some portable, 10 GPM, units for detoxifying waste lagoons. These portable units could be made available for a California demonstration.

Encapsulation
Environmental Protection Polymers

The process, according to the manufacturer, "fixes" hazardous waste for deposit in the earth. It mixes particulated contaminants with polybutadiene, a material employed for manufacturing rubber tires, and then thermosets the mixture to form a block of waste. The block is then encased in a seamless, ¼-inch thick jacket of polyethylene, a material used in jacketing electrical cable. The process, it is claimed, does not significantly increase the volume of material requiring disposal, a factor that could contribute greatly to the attractiveness of the process. The resulting product is reported by the vendor to exhibit outstanding resistance to water leaching, and chemical, physical, and mechanical stresses. Additionally, the process claims to offer the advantages of "disposing" of the waste in a manner in which it can be easily and safely retrieved.

Adsorption
Dr. Samia Fadl

The process is designed to remove hazardous materials, mainly heavy metal ions, dissolved organics, phenol and cyanides from industrial sewage. The method uses carbon to adsorb the contaminants, but rather than using activated carbon, uses low rank lignite coals, an abundant natural resource in North America.

Lignite coals cost approximately one tenth the amount for activated carbon and have been found by the applicant to be superior to activated carbon for selected contaminants. In addition to clarifying effluent, the lignite might also be useful as a source of energy when its adsorbing capacity is exhausted. The process has been tested at the bench scale using simulated wastes and is at a stage for expansion to a pilot scale.

Waste Oil Conversion
Soil Recovery, Inc.

The Soil Recovery Process is claimed to be a method of converting oily wastes such as those found in waste lagoons into an inert mass which has several useful properties. The process consists of mixing a specially adapted reagent with the waste at the site of the pond. After proper mixing, the reaction, which is exothermic, occurs and the waste is converted into a dry, hydrophobic pulverized mass. Once the waste has been converted into the solid, water-repellant material, it can either remain on the treatment site or be returned to the lagoon from which it came.

Advantages claimed for the process are 1) waste can be treated on site; 2) the treated material is environmentally safe; and 3) treated material need not be disposed of in chemical landfills. Process is claimed to be very price competitive.

Encapsulation/Coagulation
Colloid Piepho

The process is described by the vendor to utilize a one-step chemical encapsulation/coagulation system followed by filtration dewatering to clean oily and petrochemical wastewaters. Typical wastestreams for which such a process could be applicable include oily wastewaters from the metal working industries, spray booths, PCB waste from electrical transformers and waste effluents from the computer chip industry.

According to the developer, a montmorillonite based formulation is added directly to oily wastewater and agitated vigorously using a turbine mixer. The polymers disperse and as the acids and bases dissolve, polymer-oil complexes are formed and immediately covered by sodium montmorillonite. Experience indicates that most emulsions treat best if the pH is first lowered. To do this, an organic acid is chosen with a fast solubility rate and left uncoated. Other acids and bases are coated to prevent them from interfering with the lowering of the pH at this point. After sufficient time has been given for oil collection and sodium montmorillonite covering, the pH is affected by the slower dissolving acids/bases. Once again, flocculation and montmorillonite covering occurs. Another acid/base dissolves and the flocculation sequence occurs again until almost all of the oil is fixated. The mixer is turned off and conventional sludge settling and dewatering can be done. The applicant has found that most oily wastes can be effectively cleaned with one of eleven formulations commercially available.

Operational results have demonstrated that greater than 99% of its emulsified oil and other dispersed contaminants are removed. Clarified liquid is dischargeable to the sewer and the sludge generated by the system is high solids content and nonleachable.

SUMMARY

As is illustrated by the processes discussed in this paper, there are either in commercial existence or under development, many processes that appear to offer promise as answers to hazardous waste problems. It is simply no longer necessary and certainly not desireable to put highly toxic and persistent wastes into landfills without treatment. There are many options far more environmentally preferable.

There is presently underway within California a program to phase out the disposal of certain highly toxic wastes in landfills. This program was initiated by a Governor's Executive Order and seems to have broad support throughout the State. We believe that it is only a matter of time before similar approaches to waste management, i.e. treatment rather than burying, will be adopted in other industrial states. We hope that the processes discussed in this paper will accelerate these adoptions.

TABLE I. PROCESSES SELECTED FOR DEMONSTRATION

Applicant	Type of Process	Waste Streams	Description
J.K. Shah Midland Ross Corp. 900 N. Westwood Toledo, OH 43696 (419) 537-6242	Incineration/ Pyrolysis	Mixed Wastes	A thermal oxidation process for liquids and sludges which combines starved air pyrolysis with fume incineration. The process requires no particulate clean-up and achieves EPA required destruction efficiencies.
Arthur J. Helmstetter Systech Corporation 245 North Valley Road Xenia, OH 45385 (513) 372-8077	Cement Kiln Co-Combustion	Liquid Combustible Wastes	The process involves the co-combustion of liquid wastes in a cement kiln during the production of cement. Energy value of the waste is recovered directly as heat to make cement. Destruction efficiencies for the wastes involved is very high.
Ed Matovich Thagard Research Co. 2712 Kelvin Avenue Irvine, CA 92714 (714) 523-2034	High Temperature Pyrolysis	Organic Waste	The process uses radiative heat transfer in a proprietary reactor to bring about temperatures of 4000°F on the surface of waste particles. Destruction is instantaneous and complete with only combustion products remaining.
Roger D. Kuhl Energy Incorporated P.O. Box 736 Idaho Falls, ID 84301 (208) 529-1000	Fluidized Bed Incineration	Specific Organic Waste	The incineration process is a catalytic, low temperature, fluidized bed system. The system incorporates a dry exhaust gas clean-up method for the removal of process emissions.
Phillip Schaefer Zimpro, Inc. Rothschild, WI 54474 (715) 359-7211	Wet Air Oxidation	Organics in Water	The process is a method of destruction and detoxification of dilute hazardous wastewaters. The system can be used as a means to recover useable inorganics from streams containing organics and inorganics in wastewaters.
Brad Thomson Veale Tract Farms Knightsen, CA 94548 (415) 684-2193	Soil Beneficiation	Various Nontoxic Industrial Wastes	Various nontoxic solids and sludges are disked into an operating farm to improve the quality of the soil. Wastes are approved by the State and water run-off from the farm closely monitored.
Thomas G. Zitrides Polybac Corporation 1251 South Cedar Crest Blvd. Allentown, PA 18103 (215) 433-1711	Biological	Toxic Organic Wastes	Microbes have been developed to selectively break down toxic organic wastes such as 2,4-D; 2,4,5T; and some PCBs. The microbes can be added to conventional systems and are added through specialized treatment systems (CTX Treatment Systems).

Tom Creeden Pure Water Systems, Inc. 4 Edison Place Fairfield, NJ 07006 (201) 575-8750	Ultra-Violet	Organics in Water	Water containing toxic organic wastes is exposed to ultra-violet light which accelerates the degradation of halogenated aromatic compounds by naturally occurring bacteria. Process is most applicable to detoxifying on-site lagoons.
H.R. Luowitz Environmental Protection Polymers, Inc. 13414 Prairie Avenue Hawthorne, CA 90250 (213) 675-3555	Encapsulation	Toxic Non-Combustibles	The process is a technology using polymers to encapsulate extremely toxic wastes. The wastes can be either dry and unconfined, sludges, or containerized. The end result of the encapsulation process is the isolation of the waste in question for either retrievable storage or burial.
Dr. Samia Fadl Simon Fraser University Burnaby, B.C. Canada 219-3573	Adsorption	Wastewater	An adsorption technique for removing organics and metals from wastewaters using low value lignite coals. Spent coal from the process could be used as an energy source.
Joel Shofel Soil Recovery, Inc. P.O. Box 2147 95 Madison Avenue Morristown, NJ (201) 540-0566	Waste Oil Conversion	Organic Sludges	The process involves adding a reagent to sludgey wastes to produce a dry, hydrophobic pulverized mass. The resulting material which is solid and water repellent can be used as clean fill.
Rick Brinkman Colloid Piepho 5100 Suffield Ct. Skokie, IL 60077 (313) 966-5720	Encapsulation/ Coagulation	Contaminated Aqueous Streams	A one-step chemical additive system for small volumes of emulsified and water insoluble wastes.

RECOVERING METALS FROM METAL FINISHING WASTES

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ABSTRACT

This paper gives an overview of recovery methods used in metal finishing operations. It provides some details on a pilot plant designed to recover metals from waste treatment sludges and other manufacturing byproducts.

INTRODUCTION

Recycling of metals by industry is practiced at significant levels. But this practice is largely restricted to the pure, solid, scrap metal. As an example, recycled copper constitutes about 20 percent of the total copper metal available in the market. This is the scrap that needs simple melting and refining. The scrap comes from two sources: removal from capital goods such as buildings, industrial machinery, etc., or consumer goods such as automobiles, appliances, etc. as well as scrap generated in their manufacture.[1]

On the other hand, permanent metal losses are also tremendous. Of all the recorded production of copper in this country, 72.5 million short tons, about 60% are traceable as being in use presently. Forty percent or 29 million short tons (58 billion pounds) are lost permanently due to wear, abrasion, chemicals, fabrication, etc. At today's prices, this loss amounts to 58 billion dollars figured at the price of finished copper product. The loss is staggering when figured in terms of the finished capital and consumer goods.[2]

An example of this loss from chemical and metal processing is provided by the electroless copper plating industry. The printed circuit board industry comprises ten percent of all the electroplaters in business. They generated about a million gallons of liquid waste (sludges) annually. Typically, one gallon of this sludge weighs about ten pounds and contains ten percent copper, so about a million pounds of copper are contained in this sludge. Disposal of such waste is not always carried out with future recovery in mind, so a very significant amount is lost each year.

Metal-containing wastes are not treated for recovery for many reasons. Generally, recovery is not an economical proposition in terms of capital and operating costs, it is an incompatible operation, or individually the quantities generated are not large enough to justify a recovery system when evaluated simply on the economics of the metals themselves. The broader picture which includes disposal and treatment costs as well as liabilities merit additional consideration.

Regulations

Federal regulation of pollution control has been closely followed by state and local governments issuing their own wastewater and hazardous waste programs. These programs can be, and often are, more stringent than federal programs. Their basic goal has been to protect the health and safety of the general public by controlling industrial discharges of all types to the environment. This has been accomplished by increasing the degree of complication and precaution required at each waste treatment or disposal operation. This has usually come in the form of more advanced technology, often at a greater cost. Further, elimination of some

Table 1. Economic Penalty for Losses of Plating Chemicals[4]

Chemical	Cost ($/lb)			
	Replacement	Treatment[a]	Disposal[b]	Total
Nickel:				
As $NiSO_4$	0.76	0.28	0.17	1.21
As $NiCl_2$	1.04	0.29	0.24	1.57
Zinc cyanide as $Zn(CN)_2$:				
Using Cl_2 for cyanide oxidation	1.41	0.72	0.25	2.38
Using NaOCl for cyanide oxidation	1.41	1.53	0.25	3.19
Chromic acid as H_2CrO_4:				
Using SO_2 for chromium reduction	0.78	0.48	0.32	1.58
Using $NaHSO_3$ for chromium reduction	0.78	0.69	0.32	1.79
Copper cyanide as $Cu(CN)_2$:				
Using Cl_2 for cyanide oxidation	1.95	0.72	0.25	2.92
Using NaOCl for cyanide oxidation	1.95	1.53	0.25	3.73
Copper sulfate as $CuSO_4$	0.56	0.28	0.17	1.01

a Based on chemical system described in Tables 2 and 3.
b Based on Figure 1 at $0.10/gal sludge disposed.

Table 2. Chemical and Sludge Disposal Cost:Example System[a] [4]

Treatment step	Waste streams	Treatment chemicals		Sludge disposal		Total annual costs ($)
		Rates (lb/h)	Cost rates ($/h)	Dry solids generated (lb/h)	Disposal cost ($/h)	
Chromium reduction	30 gal/min = 1,800 gal/h 0.75 lb/h Cr^{+6} 0.15 lb/h Cr^{+3}	1.86 SO_2 0.36 H_2SO_4	0.18			
Cyanide oxidation	20 gal/min = 1,200 gal/h 0.80 lb/h CN^- 0.60 lb/h Zn^{+2}	5.6 Cl_2 6.4 NaOH	0.93			
Neutralization:						
Chrome effluent	1,800 gal/h	2.7 NaOH	0.22			
Cyanide effluent	1,200 gal/h	([b])	([b])			
Acid/alkali waste	60 gal/min = 3,600 gal/h	3.6 NaOH	0.29			
Precipitation	0.90 lb/h Cr^{+3}	2.1 NaOH	0.17	1.80	0.53	
	0.60 lb/h Zn^{+2}	1.2 NaOH	0.10	0.91	0.28	
	3.01 lb/h Fe^{+2}	6.0 NaOH	0.48	4.83	1.44	
	2.41 lb/h Ni^{+2}	4.8 NaOH	0.38	3.80	1.10	
	1.51 lb/h Cu^{+2}	3.0 NaOH	0.24	2.30	0.68	
Subtotal, precipitation		17.1 NaOH	1.37	13.64	4.03	
Flocculation	110 gal/min = 6,600 gal/h	0.66 polyelectrolyte	0.66			
Total		1.8 SO_2 0.36 H_2SO_4 5.6 Cl_2 29.8 NaOH 0.66 polyelectrolyte	3.65	13.64[c]	4.03	
Chemicals						17,500
Sludge disposal						19,300

[a] System described in Table 3
[b] pH adjustment not required
[c] Sludge volume at 4% solids=40 gal/h.

Table 3. Investment Cost: Example System*

Component	Cost ($)
Chromium reduction unit (continuous system rated at 30 gal/min, from Figure 2)	23,000
Cyanide oxidation unit (continuous system rated at 20 gal/min, from Figure 3)	40,000
Neutralizer (single-stage continuous system rated at 110 gal/min, from Figure 4)	28,000
Flocculation/clarification unit (continuous system rated at 110 gal/min, from Figure 5)	26,000
Polymer feed tank, mixer, and feed pump	3,000
Sludge storage tank (5,000-gal tank to provide sludge storage volume, from Figure 6)	13,000
Total equipment and installation cost	133,000
Contingency (10% of total equipment and installation cost)	13,000
Total installed cost	146,000

*References listed in table are irrelevant to this report.

Table 4. Annual Cost Summary: Example System*

Component	[illegible]
Operating labor (based on 2 h per shift)	[illegible]
Supervision	[illegible]
Maintenance	[illegible]
General plant overhead	[illegible]
Depreciation	[illegible]
Taxes and insurances	[illegible]
Chemical cost (Table 5)	[illegible]
Sludge disposal cost (Table 5)	[illegible]
Sewer fee (Figure 8)	[illegible]
Utilities (electricity) (approximately 25 hp required)	[illegible]
Total annual cost	[illegible]

*References listed in table are irrelevant to this report.

Tables 3 and 4 describe the capital and operating costs for an example waste treatment system.

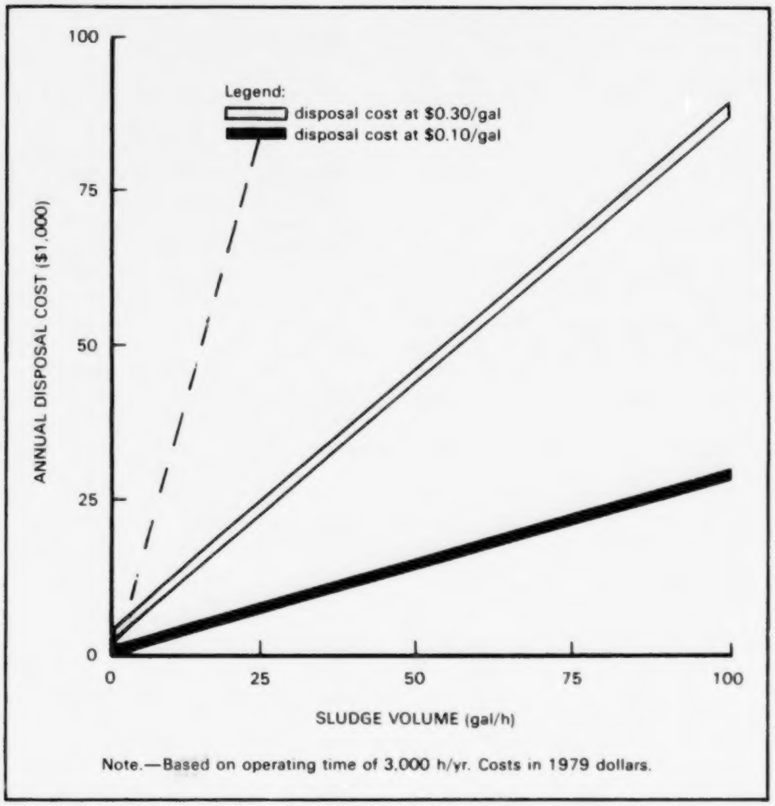

Figure 1

Annual Cost for Sludge Disposai

Figure 1 shows what sludge disposal did cost, what it costs now, or will cost in the future. The dotted line reflects the loaded disposal cost for electroplating sludges disposed in a secure landfill at $1.00/gal.

treatment options has occurred because of public opposition to landfills and incinerators, etc. Today, landfilling of metal bearing wastes is at best a difficult and costly option. It begs the question of liability if something should go wrong in the future at the landfill site. The future may show that while land disposal is today's most widely used option, resource recovery and associated detoxification is the optimum approach.

Economics[3]

Do you know what it costs?

The "whys" of pollution control have a strong economic side. Pollution is really process chemicals going down the drain. Efforts to control discharges will provide real dollar savings. Consider this, these chemicals have been bought and paid for once and now, as pollution, require additional expenditures of capital for treatment equipment and, of course, more chemicals. Further, the cost of disposal of these process and treatment chemicals carry a hefty dump fee, not to mention any contingent liability which may exist if the disposal facility fails to maintain proper disposal standards. How long will these facilities for land storage of wastes exist? As they become more scarce their users' costs will increase.

Table 1 describes what it costs to waste chemicals in 1979 dollars.[4] Capital goods have increased about 20 percent since then and the cost of disposal has increased to $0.50-$1.00/gal, far beyond the $0.10/gal used as the basis for this chart, a summary of Tables 2, 3, and 4 and Figure 1.

Table 2 describes what chemicals are used for treatment and what they cost.[4]

Tables 3 and 4 describe the capital and operating costs for an example waste treatment system.[4]

Figure 1 shows what sludge disposal used to cost, what it costs now or will cost in the future. The dotted line reflects the disposal cost for electroplating sludges disposed in a secure landfill.

These charts show that pollution costs all of us money. If the waste treatment costs are tagged onto some profit centers, some of them may turn out to be costing money to operate. Their profitability may be restored by cutting waste; that which results from inefficient operations and extravagant wastes of process chemicals. This is the subject of this paper--how to accomplish waste reduction and recovery from metal finishing operations.

METALS RECOVERY

Do An Inventory

The word recovery indicates that something has been lost and in many metal finishing plants, indeed something has. The quickest and surest way of conserving and recovering metals is to prevent them from becoming part of a mixed metal waste stream. Recover them before they are lost as pollution.

This recovery process must be started with a good inventory of your plant and its wastes generation characteristics. Review each plating tank, rectifier, hoist, steam coil or other piece of equipment; and do it in a new suit and shoes. The place you are most reluctant to go in your new clothes is probably the area that needs the most attention. Determine the actual flow of each line using the bucket and stop watch method. Review your water bills to see if your total water use inventory is consistent with what you've been buying. Chemical purchases representing a six-month period should be studied carefully. This inventory of water and chemical usage will be the beginning of identifying where the metals are exiting your process and entering the sewer. Determine how frequently dumping of process chemicals occurs and why it occurs. Contamination that could be eliminated may reduce the associated pollutant load and maintain more of the process chemicals in the process.

Equipment design and layout can be a major source of pollution if one considers how much chemical waste occurs if parts must be carried across a plant between operations. Proper work patterns can restore efficiency to an operation while further minimizing floor spills and contamination. If reorganizing the shop is not feasible, consider letting the batch of parts remain above the process for an extra 15 seconds to allow additional draining. This keeps the process solutions in the tanks; off the floor and equally important, out of other processes. Orienting pieces to facilitate drainage will also aid this process.[4]

Salvaging improperly prepared parts is expensive from several perspectives. First, the pollution has been generated during its first preparation. Stripping or reversing completed preparation processes will generate additional pollution. Then the piece has to be reworked. Look at the cause of the rework required. Is there a contaminant causing this? If so, eliminate it at the source and reduce the associated pollution caused by rework and salvage. It is of major consequence.

Conserve that which you have bought.

Conservation of these materials is a major factor in controlling pollution. Keep them out of the sewer. Many processes can be operated at a lower concentration than conventional wisdom would have you believe. Experiment with this possibility and pursue it with any and all knowledgeable people; including your suppliers. Chemical substitutions play a role here. Will a chloride bath do just as good a job as a cyanide bath? If so, you've just conserved $10-40,000 worth of a cyanide waste treatment system.[5]

Water conservation will help conserve other things as well. In plating, counterflow rinsing is a monumental step towards conserving chemicals and water. The concept can be applied to other uses of chemicals. Basically, use a chemical more than once if you can and then recycle it; e.g., use sulfuric acid for steel pickling and then reuse it to neutralize a caustic stream. Flow restrictors can further reduce water usage where counterflow rinses have been installed or where room is insufficient for additional tanks. A three-stage counterflow rinse can recover about 90 percent of the chemicals which would be lost in a single stage rinse. Spray and timed rinses can also be of major consequence for water saving.

Only after rigid water and chemical conservation at the point of generation is a common practice, should one begin to consider recovery equipment as part of the process. The cost of any piece of treatment equipment will be some function of its hydraulic capacity. The bigger the flow, the greater the capital cost and floor space requirement.

> "It is extravagant and often futile to consider any recovery process equipment until the maximum flow reduction has been achieved in each and every operation that has recycling potential. The best and most reliable way to specify any recovery method is by measuring the flow and assiduously monitoring and analyzing the wastewater in concern. Without specific data, equipment may be recommended purely on speculation, thus increasing the possibility of under- or over-design. The latter is not a functional disaster--just a waste of money. Conversely, under-design will spur financial and emotional problems in that the recovery system will be expected to perform in ways never intended. Again, complete your water conservation program and then consider and select the appropriate treatment technology for the specific applications in your plant."[6]

IN PROCESS RECOVERY SYSTEMS

Recovery equipment should be chosen with the understanding that it can be a money saver but that it is a piece of process equipment just like any other chemical system. It will not operate by itself but must have some form of maintenance and operational attention. Diminished waste treatment and sludge disposal costs should be factored into the equation as, you recall, we are going to look at the plating line as a profit center and take into account the total cost of its operation.

The least expensive and the most cost effective recovery system is a simple drag-out tank. The first rinse is a still rinse which recovers much of the material from the plating bath which is dragged out. If the plating bath is above ambient temperature, the drag out or dead rinse tank contents can be used to restore the plating bath level. Impurity control is important in both tanks so extra makeup water purification is essential.

Ion exchange uses polymeric resins which remove metal ions from wastewater by exchanging them for ions already in the resin. These metal ions eventually saturate the resins and they must be regenerated usually by replacing the metal ions with sodium from brine solutions or hydrogen from acid solutions. Anions can also be captured in resin columns of the appropriate material. They are restored with caustic. These recovered solutions may be added back to the plating tanks, however the volume tends to grow which limits its use to hot baths or where evaporation can be used to further decrease the amount of solution.

In electrodialysis--basically electrolytic dialysis--ions move through membranes which only allow the passage of only either anions or cations. By stacking these membrane types alternately and applying a DC current, the ions in the waste streams are forced to migrate from the dilute-wastewater so as to form a series of channels into collecting-concentrating-channel where it is available for reuse. The greater the concentration, the greater the efficiency of the system. Its best applications are where dragout is high.

Reverse osmosis is used for the removal of dissolved organic and inorganic materials and control of such wastewater parameters as soluble metals, TDS, and TOC. It separates dissolved materials in solution by filtration through a semipermeable membrane at a pressure greater than the osmotic pressure caused by the dissolved materials in the wastwater. With existing membranes and equipment, operating pressures vary from atmospheric to 1,500 psi. Products from the process are (1) the permeate or product stream with dissolved material removed, and (2) concentrate stream containing all removed material. Removal levels obtainable are dependent on membrane type, operating pressure, and the specific pollutant of concern. Removal of multicharged cations and anions is normally very high, while most low molecular weight dissolved organics are not removed or are only partially removed.

Distillation is one of the simplest methods of separating plating chemicals from water. The distilled water is condensed in a chiller. Distillation can be accomplished at ambient temperatures but is less likely to destroy heat sensitive chemicals if accomplished under a vacuum, i.e., at a lower boiling point. Fabrication of equipment should be made with considerations of the corrosive environment caused by the materials being recovered.[7]

Metal Recovery from Hydroxide Sludges[8]

Treatment of hydroxide sludges for metal recoveries falls into two categories: wet and dry. In wet processes, separation reactions are carried out usually at atmospheric temperatures and pressures. In dry processes, separation reactions take place at elevated temperatures. The former processes are generally classified as hydrometallurgy and the latter as pyrometallurgy.

Pyrometallurgical treatments for segregated single metal sludges are:

- Direct smelting after dewatering,
- Direct alloying with other metals.

For economical feasibility, the operation of pyrometallurgical processes would have to be on a very large scale, and requires concentrated feed material. The mixed metal hydroxide sludges fail to meet these two requirements. But, pyrometallurgical treatment using the two above bulleted processes are presently available.

Hydrometallurgical treatments for mixed and segregated sludges use aqueous dissolution of metals by leaching followed by recovery of individual metals or metal compounds from this solution.

There are certain advantages for using hydrometallurgical processes. Metals may be removed directly from the solution by concentration, electrolysis, or hydrogen reduction. Fuel requirements are low as the processes are carried out at low temperatures. Disadvantages are that solution purification and concentration upgrading may be absolutely necessary before metal recoveries are possible.

The hydrometallurgical treatment of the hydroxide sludges requires that the process be specific, reproducible, and controllable.[9] The process should also be possible with a minimum number of unit operations and/or unit processes. Those needed depend on the chemical state and also on the physical environment of the metals. Electroplating wastes, after the hydroxide neutralization, will consist mainly of metal hydroxides such as $Cu(OH)_2$, $Ni(OH)_2$, $Cd(OH)_2$, $Zn(OH)_2$, etc. With lime neutralization, the sludge will also contain calcium salts.

Solvents for these metallic constituents are sulfuric acid, ferric sulfate, ammonia and ammonium carbonate, sulfur dioxide, ferric chloride, hydrochloric acid, and nitric acid and are used to solubilize metal ions. The order given is about that of their importance. Metal recovery from these solutions by such operations as cementation (coprecipitation with or solution substitution by another metal) or electrolysis is most commonly practiced from the metal sulfate solution.

Sulfuric acid is the most important leaching reagent. The main advantages for its use are the cost, minor corrosion problems, and dissolution of many metal forms. Its main disadvantage is that it sulfatizes everything, which does not provide any selectivity. Ferric sulfate may be obtained cheaply from spent pickle liquors. Its primary function is to provide a sulfate solution. Ammonia and ammonium carbonate may be suitable reagents for some hydroxide sludges because they possess better selectivity for solubilizing metal constituents in a hydroxide sludge. But the reagent cost is very high and their recovery in the process would be mandatory from an economical point of view.

The primary aim for a solvent is to bring the metal or metals into solution from which individual separations can provide pure solutions, with major impurities removed.

Leaching of hydroxides by either sulfuric acid or ammonia will provide dilute solutions. Copper may be recovered from lean sulfate solutions by cementation with iron, displacing copper quantitatively from a solution. The product, called cement copper, although rich in copper, may be highly contaminated with iron so that only a smelter may be able to handle it.

A technique which is becoming widely accepted for concentrating solutions is one of ion exchange. The ion exchange medium may be solid or liquid. Generally speaking, concentrating by solid organic resins is known as ion exchange (IX) and by liquid organic resins is known as solvent extraction (SX). Ion exchange has tremendous applications in uranium metallurgy as the solvent extraction technique is becoming accepted in copper metallurgy. Its acceptance is on such a large scale that the future may see its application in areas where the ore grade has decreased or residual metallic wastes are to be treated as in this case.

For sulfuric acid leach solutions, copper may be recovered from the polymetal solution by cementation under oxidizing solution. The cement copper may be sold directly to a smelter or releached for electrolysis. Other metals are selectively precipitated after iron removal and may be recovered as pure metals or metal compounds. Electrolysis regenerates the sulfuric acid for recycle which is a very important factor in economic evaluation because regeneration is part of the process requiring no additional or extra regeneration equipment installation.

Copper may also be removed from the polymetal sulfate solution by solvent extraction and strip copper then is removed by electrolysis. Other metal recoveries may be achieved by further solvent extraction or by cementation with zinc.

If an ammonia leach is employed, metals such as copper, nickel, and zinc are selectively brought into solution as amines from the hydroxide sludges. Other impurities such as iron and calcium are left behind as solids. Copper may be removed from this polymetal solution by solvent extraction, stripping with sulfuric acid, and electrowinning. Other metals are further treated for separation. Additional reagent recovery equipment is necessary.

Generally, there are three types of liquid wastes in a plating shop: (1) rinse waters, (2) spent baths, and (3) spills.

Spent baths are collected separately. They require only cyanide destruction and thus become concentrated metal solutions. Rinse waters and spills are treated conventionally by heavy metal precipitation. This presorting provides two distinct feed materials: (1) a concentrated solution, and (2) a hydroxide sludge. The leach solution from hydroxide sludge leaching with sulfuric acid is mixed with the spent bath solution for metal extraction.

Metals conservation and recovery has economic, environmental, and socio- political benefits. The recommendations made in this paper will help to alleviate some of the economic consequences of waste treatment, reduce environmental impacts from this industry, and reduce the rate at which permanent metal loss occurs.

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EPA MINING WASTE RESEARCH

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INTRODUCTION

The mining industry generates an estimated 2.3 billion tons of solid waste each year. Historically, the total accumulated solid waste from both active and inactive mine sites approaches 30 billion tons. Five segments of the mining industry generate 85 percent of mine solid waste: copper, phosphate, iron, uranium, and coal.

In recent years, Congress has passed three acts indicating increasing interest in the proper disposal of solid waste generated by the mining industry. The Reource Conservation and Recovery Act (RCRA) is the most comprehensive regulatory authorization. It was passed in 1976. RCRA is implemented and enforced by the Environmental Protection Agency (EPA) and is intended to control municipal and industrial solid wastes. The passage of the Surface Mining Control and Reclamation Act (SMCRA) of 1977, implemented and enforced by the Department of Interior, controls coal surface mining and the surface effects of underground coal mining. The Uranium Mill Tailings Radiation Control Act (UMTRCA) of 1978 is implemented by EPA and enforced by the Nuclear Regulatory Commission (NRC) to control uranium mill tailings disposal.

RCRA

The Resource Conservation and Recovery Act addresses the disposal of waste from municipal or industrial sources. Specific to mining, RCRA recognizes the special problems associated with this industry, and requires that a special study be made. This study will be discussed later. Two types of mining waste which are exempted from control under RCRA are uranium mill tailings (covered by UMTRCA) and overburden intended for return to the mine site (except when specifically included by EPA).

The basic regulatory philosophy underlying RCRA is that wastes are one of two types: either hazardous or nonhazardous, and the regulatory scheme applicable to each type is different. Hazardous wastes are those currently listed by EPA in its Section 3001 regulations or those which fail specified tests for toxicity, corrosivity, reactivity, and/or ignitability. Wastes which are not listed by EPA and which do not fail the tests for these four characteristics are presumed to be nonhazardous.

Hazardous wastes are regulated under a "cradle-to-grave" approach. The generator, transporter, storer, treater and disposer are all subject to regulation. The regulations provide a manifest system to track the waste from the point of generation to the point of ultimate disposal. Specific standards are set for transport, treatment, storage, and disposal. In addition to the technical standards, administrative standards covering recordkeeping, reporting, and financial responsibility are also imposed.

Presently, EPA's RCRA Subtitle C regulations do not apply to mining wastes. Congress amended RCRA on October 21, 1980 so that solid waste generated from the "...extraction, beneficiation, and processing of ores and minerals..." are excluded from regulation under Subtitle C. Subtitle C does however, have important implications for the mining industry. While no mining wastes are included in the RCRA control system now, EPA may eventually bring these wastes under regulation. It is important to note that the RCRA mining wastes exclusion is not a permanent exclusion. At the same time Congress excluded mining waste from RCRA subtitle C regulation, Congress directed EPA to perform a special study of the mining industry and waste generated from mining operations. EPA can, if it determined it necessary, issue RCRA Subtitle C regulations for the mining industry six months after it completes this study. The mining exclusion would end if and when EPA issues Subtitle C regulations. EPA views mining wastes as "special wastes." That is, unlike many low volume, high toxicity waste streams regulated under RCRA (and for which Subtitle C of RCRA was designed), most mining operations produce high volume, low toxicity waste streams. Obviously, EPA could never apply its existing RCRA Subtitle C regulations to these waste streams. If EPA decided there was a need to control the disposal of mining waste, the RCRA regulations it would issue would be custom fit to the mining industry and the unique nature of wastes generated from mining operations.

SMCRA

The Surface Mining Control and Reclamation Act applies to coal surface mining and the surface effects of underground coal mining. Interim and permanent regulatory programs have been promulgated by the Department of the Interior to implement the authority of that law. The regulations include specific requirements for the construction and operation of mine waste disposal sites, including both mining and processing wastes. The requirements are intended to prevent the formation of acid mine drainage and other adverse environmental conditions, and assure that the mine site is returned to a condition as good or better than before mining. Monitoring of surface water and groundwater is provided in the regulations. The Department of the Interior requires the posting of a bond to provide the funds to reclaim lands damaged by mining operations, and has the power to shut down mine sites which do not comply with its regulations.

UMTRCA

The Uranium Mill Tailings Reclamation and Control Act requires the promulgation of standards for the disposal of both radioactive and nonradioactive mill tailings at both active and inactive sites. The standards are to be promulgated by EPA, but the Nuclear Regulatory Commission (NRC) is the enforcement authority, through its permitting procedure for uranium mining operations.

SPECIAL STUDY - MINING WASTE

Authority

Section 8002(f) of RCRA requires that EPA conduct a special study of the wastes generated by the mining industry. The requirements of this study are delineated in the following excerpt from RCRA:

> "The Administrator, in consultation with the Secretary of the Interior, shall conduct a detailed and comprehensive study on the adverse effects of solid wastes from active and abandoned surface and underground mines on the environment, including, but not limited to, the effects of such wastes on humans, water, air, health, welfare, and natural resources, and on the adequacy of means and measures currently employed by the mining industry, Government agencies, and others to dispose of and utilize such adverse effects. Such study shall include an analysis of -
>
> (1) The sources and volume of discarded material generated per year from mining;
> (2) present disposal practices;
> (3) potential dangers to human health and the environment from surface runoff of leachate and air pollution by dust;
> (4) alternatives to current disposal methods;
> (5) the cost of those alternatives in terms of the impact on mine product costs; and
> (6) potential for use of discarded material as a secondary source of the mine product."

Scope of Study

EPA's Office of Solid Waste (OSW) requested that the Office of Research and Development (ORD) help it conduct the mining waste study required by Congress. Due to the time constraints imposed by Congress and the lack of available data concerning these wastes, ORD was forced to approach the problem at two different levels. Phase I consisted of an exploratory investigation of 45 mining sites to evaluate the solid waste disposal practices currently being utilized by the mining industry. Phase II is comprised of a presurvey which included collecting mine waste samples from 65 active and abandoned mines and detailed environmental evaluations at eight of these sites.

Phase I

Phase I consisted of a survey of current solid waste management practices. The selection of the management practices to be studied in Phase I was based on the volume of solid wastes produced and their potential for causing harm to the environment.

A Mine Solid Waste Coordinating Committee (MSWCC) was established (consisting of representatives from the EPA Regions, the Office of Solid Waste, Effluent Guidelines Division, the Office of Research and Development, and other Federal Agencies including the Bureau of Mines, Geological Survey, Fish and Wildlife Service and Soil Conservation Service) to assist the Agency in selecting the management practices to be evaluated during the entire study. The American Mining Congress and the Interstate Mining Compact Commission also participated on the committee in an advisory capacity.

This committee nominated candidate mines that utilized solid waste management practices that were representative of the industry. EPA compiled the list and selected forty five mines for final review and selection.

Based on information obtained from published literature, interviews with industry representatives, reports and research of Federal and state agencies, onsite visits to the forty five mines, and information supplied by EPA, a listing of types of management practices for the disposal of solid waste from mining and beneficiation processes was derived. Management practices from the following industries were considered:

1. Metallic ore mining and beneficiation (e.g., copper, lead, zinc, molybdenum, gold, and silver).
2. Phosphate ore mining and beneficiation
3. Uranium mining

The evaluation of each practice was based upon the following criteria: (1) protection of public health and welfare, (2) protection of the quality of ground and surface waters from leachates, (3) protection of the surface waters from runoff, (4) protection of air quality, e.g., from fugitive dust, (5) and aesthetics.

Evaluation of each of the practices was based on visual observation; discussions with the mine operator and regulatory agencies; and data available from mine operators, literature, and regulatory agencies. No sampling or analysis of water, air, or solid waste was conducted.

The results from this phase of the study provided input to Phase II and will also be used in the preparation of the final report for the entire study.

Phase II - Presurey

Sixty five mines were visited during the presurvey. These sites were selected from a list of candidate sites suggested by the Mine Solid Waste Coordinating Committee and from the results of the Phase I study.

During the presurvey, samples were collected from active, inactive, and abandoned waste management practices. Depending on the specific site surveyed, the following residuals were sampled and analyzed: mine waste, which included overburden, waste rock, and development rock; tailings, including fresh tailings, backfilled tailings, settled solids, water, and dike material from tailings ponds; low grade ore; heap leach material; mine pumpout water and settled solids from mine pumpout water; and stockpiled topsoil. In addition, when waste materials of a certain type were segregated for disposal by separate waste management practices (e.g., backfilled and surface impounded tailings), each portion was sampled separately. The sampling protocol and the sampling equipment specified in the "Sampling and Analysis Manual", prepared for this study and approved by EPA, were used. Over 400 samples were collected from the 65 mine sites during this sampling effort.

A composite sample consisting of five to ten subsamples and totalling approximately ten pounds was collected from each management practice sampled. The subsamples were collected in a manner which assured that the most representative sample was obtained. Typically, samples were taken along a transect or from randomly selected areas of the disposal site. There were exceptions made to the sampling protocol due to physically limiting factors such as extremely steep slopes and flooded or unstable areas which prevented the safe acquisition of the samples. In these instances the selection of an appropriate sampling method was left to the discretion of the sampler. Subsamples were taken using an aluminum hand scoop from a depth of one foot; however, when physical limitations, such a frozen ground, prohibited sampling at this depth, the sample was taken from a more shallow excavation. Material that was too large to sample in this manner was reduced to a more manageable size with a crack hammer. Samples were placed in appropriately labeled one-gallon polyethylene containers for subsequent shipment.

Samples of fresh tailings were taken using a one-liter polyethylene bottle attached to an extension pole or, if possible, by filling the one-gallon sample bottle directly from the mill discharge or the tailings pond influent. A minimum of one gallon of sample was collected. An additional gallon was collected if the solids content of the tailings appeared to be excessively low.

Liquid samples from tailings ponds or mine pumpout ponds were obtained by compositing five to ten subsamples taken along a transect across the pond when possible or from the perimeter when a transect was not possible. Subsamples were collected in two one-gallon polyethylene containers and subsequently homogenized and transferred to appropriately labeled smaller sample bottles and preserved for subsequent analyses.

Samples of settled solids were taken at the same locations as the liquid samples from tailings ponds and mine water pumpout ponds. Samples were taken with a core sampler, cork and bottle sampler, or a scoop, depending on the consistency of the solids.

Duplicate samples were provided to the mine site personnel on request.

Analytical Procedures

Analyses were performed on the samples both in the field and the laboratory. Field analyses included alkalinity, acidity, conductivity, temperature, and pH, and were conducted according to procedures prescribed in "Methods for Chemical Analysis of Water and Wastes," U.S. EPA-600/4-79-020, March 1979. Samples for laboratory analysis were shipped to the contractor's laboratory. Subsequently, selected samples and aliquots of samples were forwarded to subcontractor laboratories for specific analyses. Standard chain of custody procedures were employed in all shipments.

Solid samples were subjected to total digestion, RCRA's Extraction Procedure (EP) toxicity test with acetic acid, and RCRA's EP using deionized water. Analyses for radionuclides were performed on all solid and liquid samples from the phosphate and uranium industries, on a selected small population of solid samples from the metal mining industries, and on RCRA Extraction Procedure extracts when the solid sample contained a significant level of radionuclides. Quality assurance procedures approved by EPA were adhered to for both the field and laboratory analyses to ensure both the precision and accuracy of the results.

Summary of Results

The results of the Phase II presurvey waste characterization study show several important findings:

Extraction Procedure Analysis

- As expected, a number of the waste streams analyzed exhibited elevated levels of certain parameters such as copper, lead, cadmium, selenium, and mercury. However, the concentrations of these parameters for the majority of the samples tested were considerably lower (in some cases less than detection limits) in both the acid and water extracts. In fact, no sample tested exhibited toxicity based on the results for deionized water extracts, and only 12 samples out of 300 tested (4 percent) were judged toxic as a result of lead concentrations based on the results for the acetic acid extract tests. These results suggest that in a neutral or a slightly acidic environment, most of the mining wastes tested have a relatively low leachability potential.

- Of the 12 samples tested in this study which had toxic extracts from the EP test, 9 were tailings, 2 were mine waste, and one was settled solids from a mine water settling pond.

Radionuclide Analysis

- All liquid and solid samples collected from metal mining operations exhibit levels of radium 226 less than 5 pCi/g of solid sample and 50 pCi/l of liquid sample. Concentrations of radium 226 in the acid and water extracts of these samples were less than 1 pCi/l of the extract.

- As expected, levels of radium 226 in wastes collected from phosphate mining operations were higher than the values recorded for samples from metal mining operations. The levels, however, were still relatively low with values ranging from 0.1 to 25 pCi/g of the solid samples

- Levels of radium 226 in some of the samples collected from the uranium industry were elevated. Highest values were detected for settled solids from mine pumpout water ponds (most values ranged from 90 to 250 pCi/g) and low grade ore (values ranged from 37 to 150 pCi/g of sample). Samples of overburden and segregated mine waste exhibited much lower concentrations of radium 226. Most values were within a range of 1 to 10 pCi/g of sample and no sample exceeded 50 pCi/g.

Corrosivity (pH)

- Copper leach liquor was the only sample type that exhibited the characteristic of corrosivity. Three samples of this material were collected and the pH values of these samples ranged between 2.1 and 1.9.

Phase II - Comprehensive Monitoring

Shortly after the completion of the sixty five site visits the comprehensive monitoring program was initiated. A total of eight management practices were selected for this phase of the study:

- Florida phosphate combined mine waste and clay slimes disposal--Agrico's Fort Green Mine.
- Southwest copper tailings pond--Cyprus Pima's Pima Mine.
- Southwest copper dump leach--Kennecott Copper's Chino Mine.
- South Dakota gold tailings pond--Homestake's Blackhills Mine.
- Nevada gold tailings pond--Newmont's Carlin Mine.
- Missouri lead tailings pond--St. Joe's Viburnum Mine.
- New Mexico uranium mine water pond--Kerr McGee's Churchrock #1 Mine.

- Idaho phosphate waste rock dump--Stauffer's Wooley Valley Mine.

Specific research plans have been developed for evaluation of each of the waste management practices at these sites. The plans include the design of the monitoring system (air, surface water, groundwater and climatological); sampling methods, equipment, scheduling, and handling; quality assurance procedures; mine solid waste evaluation criteria; and data handling and analysis procedures.

Monitoring and sampling during this phase of the study will continue for up to a 12-month period, and samples will be collected during four to six separate sampling periods. After the initial sampling period at each site, the sampling program may be modified due to the absence of specific parameters, inappropriate sampling frequency, or other inadequacies of the initial site-specific research plan. Monitoring at each site will include several or all of the following activities:

Surface Runnoff and Seepage: When flow is present, samples will be taken prior to exposure to solid waste material and after exposure to solid waste. Inflow records will be maintained.

Storm Event Runoff: During storm events, runoff samples will be collected on an hourly basis. Continuous flow measurements will be taken during the storm.

Climatological Data: A continuous record of precipitation, relative humidity, temperature, and wind direction and magnitude will be collected where appropriate.

Groundwater Samples: Representative samples will be collected from monitoring wells at a predetermined frequency. A continuous record of water level will be obtained when appropriate and other tests will be performed when it is necessary to define groundwater movement.

Solid Waste Samples: At several sites, representative samples of solid waste will be subjected to the EPA EP extraction procedures and the extract will be analyzed. Samples will be composited from core borings at each site and will be analyzed.

Fish and Wildlife: At selected sites a fish and wildlife-related assessment will be made. This will include literature searches, compilation of properties of toxicity, mobility, and/or bioaccumulation of selected materials, or the identification and elaboration of a specific situation of interest such as beneficial effect on fish and wildlife resulting from a specific waste management practice.

CURRENT STATUS

It is anticipated that all of the monitoring stations will be in place by the end of January 1982. Sampling and analysis has been initiated at seven of the sites and will be completed during the summer of 1982. At the conclusion of the comprehensive monitoring phase of the study, a detailed final report will be prepared describing all the results of the mining solid waste study. EPA will use this data, as well as the results from the studies as a part of a final report to Congress fulfilling the Agency's mandate under Section 8002(f) of RCRA.

CHEMICAL TREATMENT OF PCBs IN THE ENVIRONMENT

by

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ABSTRACT

During the 50 years that PCBs were manufactured and used in this country, an estimated 400 million pounds of these chemicals entered the environment. The primary sources of PCBs in the environment are the disposal of waste chemicals by consumer industries and of the waste products of municipal treatment plants. In recent years, PCBs and other hazardous chemicals have been discovered as contaminants at sites throughout the country. Conventional waste management methods cannot be used, in many cases, for in-situ treatment of contaminated soils.

The EPA has initiated studies to determine the efficacy of sodium polyethylene glycolates (NaPEG) as reagents for decomposing PCBs and other halogenated materials in the environment. The overall objective of these studies is to demonstrate that NaPEG, in less-than-stoichiometric proportions, can be applied as spray-on reagents for treatment of chemically contaminated areas. This report summarizes research aimed at development of NaPEG for the detoxification/destruction of halogenated chemicals in the environment.

INTRODUCTION

During the past ten years, newspapers and scientific journals have reported the discovery of discarded hazardous and toxic chemicals at sites throughout the country. In addition to these, the Environmental Protection Agency (EPA) has identified a group of materials that have been manufactured on a large scale during the past several years and that are now known to be harmful to living organisms, to be resistant to biodegradation and to accumulate in the food chain. Because of their toxicity, some of these materials have been removed from the marketplace. These materials must now be detoxified or disposed of in an environmentally acceptable manner. A partial list of priority chemicals scheduled for detoxification includes aldrin, kepone, benzidine, DDT, dieldrin, dioxin-contaminated materials (2,4-D, 2,4,5-T), endrin, and polychlorinated biphenyls (PCBs). Many of the current disposal methods are not adequate for environmental control of these chemicals. Efforts are therefore underway to develop effective treatment methods.

Disposal of PCBs

PCBs are among the most widespread synthetic chemical contaminants in the environment. During the 50 years that PCBs have been manufactured and used in this country, more than 400 million pounds of these chemicals have entered the environment. The primary sources of PCBs in the environment are the disposal of wastes by consumer industries and disposal of the products in municipal treatment plants. Several disposal practices have contributed to environmental contamination (Figure 1):

- Open burning or incomplete incineration of municipal and industrial waste.

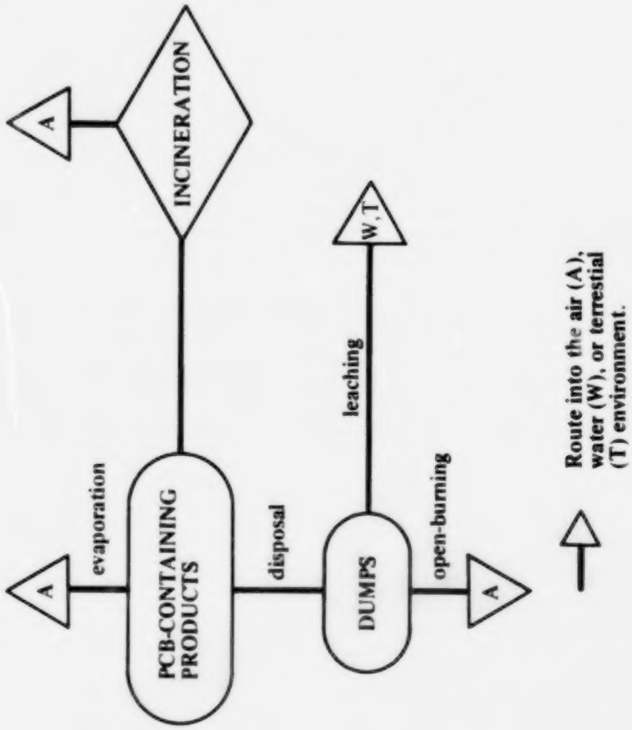

Figure 1. Common routes of environmental contamination by PCBs(1)

- Discharge of PCB-containing fluids into waterways with municipal and industrial water effluents.

- Dumping of sewage sludge, solid waste, and sludge spoils at sea and into sanitary landfills or dumps. (2)

There is general agreement that atmospheric transport is the major mode of global dispersal of chlorinated aromatic compounds such as pesticides and PCBs. The compounds are volatilized into the atmosphere and can be carried thousands of miles from the original source, either vaporized or adsorbed onto dust particles. Pesticides and PCBs have been found in ice samples collected in Arctic and Antarctic regions. (3)

Mason and Hanger (4) report that vent gas from an ordinary landfill site near Chicago contained 3240 ng/m^3 of PCBs. Also, air samples taken by the New York Department of Environmental Conservation from an uncontrolled dumpsite north of Albany showed PCB concentrations of 300,000 ng/m^3. Studies by Eisenreich, (5) Murphy, (6) and Bidleman (7) have confirmed that precipitation events (rain and snow) are the means of net transfer of PCBs from the atmosphere to large bodies of water. Volatilization of PCBs is the principal reason for concern over the use of landfills or lagoons for ultimate disposal of waste PCBs or PCB-contaminated materials.

Current PCB Waste Management Practices

The chemical stability of PCBs precludes their destruction by conventional refuse incineration methods. (8) Most municipal incinerators cannot achieve the high temperatures necessary to destroy PCBs in refuse. The surprisingly high volatilization rates of PCBs and other chlorinated aromatic compounds raises questions over the use of land disposal for these materials. Further, many landfill disposed PCBs may be recovered and destroyed by chemical treatment or high temperature incineration in the future.

Currently, some commercial chemical and physical methods are used to chemically alter or remove PCBs in PCB-contaminated oils. These methods include an adsorption system developed by RTE Corporation. The chemical methods, developed by Acurex, Goodyear, and SunOhio, involve dispersion of metallic sodium in oil or the use of sodium-biphenyl or naphthalene mixtures. Because of the reactivity of sodium with water, these reagents cannot be used efficiently to decompose PCBs in soils, sludges, and sediments, and dredgings.

Biological treatment of PCBs and other hazardous pollutants is also receiving attention. Cytox, Flow Laboratories, and Sybron Biochemical are some of the companies marketing strains of bacteria that reportedly degrade PCBs and other hazardous pollutants.

Although it has been demonstrated that biological systems can decompose phenols, fats, waxes and other organics, many skeptics remain unconvinced that microorganisms can reliably decompose highly chlorinated isomers of PCBs or other highly halogenated pollutants.

New Dehalogenation Reactions

Scientists at the Franklin Research Institute began a study 3 years ago to devise a reaction system that would lead to the cleavage of carbonhalogen bonds. Such a reaction must be rapid, complete, exothermic, and self-sustaining. After extensive study, the investigators have identified a promising chemical reagent for this purpose, prepared from sodium, polyethylene glycols, and oxygen. The EPA is supporting further research, which has been broadened to explore application of dehalogenation reagents for treatment of soils and lake sediments as well as oils contaminated with PCBs or other halogenated compounds.

Typically, the dehalogenation reagent is prepared by reaction of 60 grams of sodium with 1.0 liter of polyethylene glycol with an average molecular weight of 400. The molar ratio of sodium to solvent should be 1.1:1.0. About one-half hour after the sodium has melted, the NaPEG reagent preparation is complete.

An important feature of the NaPEG reagent is that dechlorination can be readily controlled by several parameters:

- Temperature: high temperature favors rapid and complete dechlorination.

- Reactivity: addition of water increases reaction times and reduces the degree of dechlorination.

- Concentration of O_2: dehalogenation can be stopped at any time by eliminating O_2 from the system.

- Quantity of NaPEG reagent: excess sodium or other cation ions must be present to react with liberated halogens.

Kinetic studies have been conducted on the model compound, 1,3,5-trichlorobenzene, using 6% by weight of the reagent. In all cases, the dechlorination rate was first order with respect to the chlorinated compound. (9)

Also, a kinetic study of the dechlorination of dichlorobiphenyl (DCB) was carried out at a single temperature, 59°C. When DCB was treated with the NaPEG reagent, the first-order kinetic rate constant was 0.1396 min^{-1}, with a correlation coefficient of 0.9874. After 1 hour, the reaction ceased completely. At that point, approximately 30% of the DCB added to the reaction system had been dechlorinated.

Pytlewski (9) has proposed mechanisms for dechlorination using NaPEG.

MECHANISMS

The mechanisms proposed by Pytlewski involve nucleophilic substitution and oxidative dehalogenation of halo-organic compounds. Alkoxides and hydroxides are potent nucleophiles that can dehalogenate even the least activated halogenated aromatic compound. (10)

Hydroxide and alkoxide ions displace halides of halogenated aromatics to yield phenols and aromatic ethers, respectively. The two reactions that take place are as follows:

$$\underset{\text{Arylhalide}}{AR\text{-}X} \; + \; \underset{\text{Hydroxide}}{OH^-} \; \text{-----} \; \underset{\text{Arylhydroxide}}{AR\text{-}OH} \; + \; \underset{\text{halide}}{X^-}$$

$$\underset{}{AR\text{-}X} \; + \; \underset{\text{Alkoxide}}{RO^-} \; \text{-----} \; \underset{\text{Arylether}}{AR\text{-}OR} \; + \; X^-$$

The displacement of a chloride ion from a chlorinated aromatic structure (i.e., PCBs) is rapid only if the reagent such as peroxide, hydroxide, alkoxide, or glycoxide is in the same phase as the aromatic substrates. The NaPEG reagents are miscible with halogenated aromatics in general and possess activated nucleophilic groups (RO^-, NaO_2) capable of displacement of unactivated as well as activated halides under realtively mild conditions.

The important component of the NaPEG reagent is the sodium salt of long chain polyethylene glycols. As proposed, the sodium cation is complexed by the long chain polyethylene glycol as shown in (Figure 2). Activation of the terminal alkoxide group is due to the lack of ion pairing and anion solvation. The alkoxide group is associated with electron abstraction from atmospheric oxygen, and in the generation of nucleophiles. The free radical signals of the superoxide ion in NaPEG have been measured by Electron Spin Resonance in concentrations of 10^{-3} M.

Roberts and Sawyer (11) report the degradation by superoxide ion of carbon tetrachloride, chloroform, methylene chloride, and p,p,-DDT in aprotic media. They describe the overall reactions as multistep processes and discuss the reactant product stoichiometry.

By-products of the reaction are salts and hydroxylated biphenyl derivatives. Ongoing NaPEG studies will attempt to demonstrate that less-than-stoichiometric proportions of NaPEG can be applied to clean chemically contaminated facilities, soils, and other materials. Specifically, the studies will attempt to demonstrate that the removal of one Cl^- is all that is required for subsequent degradation of the hydroxylated structure by naturally present soil microorganisms.

Applications of NaPEG Reagents

In laboratory studies, NaPEG reagents reduced PCB concentrations of dielectric fluid from 1000 ppm to less than 1 ppm and in soils from 1000 to 481 ppm. (9) Conceptually, since NaPEG dehalogenation mechanisms are not based on a dispersed metallic sodium reaction, the reagent can be used to treat contaminated soils, dredgings, sediments, and low-moisture sludges to remove organohalogens.

A proposed procedure is being evaluated for treatment of low-moisture 15-20% PCB-contaminated waste. In two established experimental studies at Appleton, Wisconsin and Coventry, Rhode Island, soil contaminated with PCBs (42 to 200 ppm) is spread over a heat-adsorbent liner (PVC) to a depth of 12 inches. The NaPEG reagents, which are very viscous, are diluted with isopropyl alcohol, and sprayed in less-than-stoichiometric proportions (0.5 M NaPEG/1.0 M PCBs) onto the contaminated soils.

Soil samples including controls and a standard (approximately 200 ppm) are taken before treatment and at intervals of 15, 30, 60, 90, and 180 days after treatment. The treated areas are covered with a liner throughout the study to prevent the introduction of excess water from rain or snow precipitation. It is hoped that this investigation, scheduled for completion in June 1982, will prove the method to be more cost-effective for PCB control than conventional decontamination procedures such as incineration or containment.

CONCLUSION

Conventional chemical treatment of halogenated compounds necessitates the exclusion of moisture and air from the reaction. Detoxification of PCB-contaminated soils and sediments by conventional methods would be extremely costly and cumbersome, particularly on a commercial scale. A new chemical reagent has been developed in the laboratory that requires oxygen and tolerates low amounts of moisture which could facilitate treatment. A reactive reagent is prepared from sodium, polyethylene glycols, and a continuous supply of oxygen. In laboratory studies, the NaPEG reagents have successfully reduced the PCB level of contamianted oils and soils from 1000 ppm to less than 1 ppm. The continued success of ongoing field and laboratory studies could lead to a viable method for destruction of PCBs, chlorinated pesticides, dioxins, and other toxic organohalogens dispersed in the environment.

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DESTRUCTION OF HAZARDOUS WASTE USING SUPERCRITICAL WATER

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ABSTRACT

MODAR has developed a new process that is capable of destroying highly toxic wastes with efficiencies of greater than 99.99%. The process uses supercritical water as the processing medium for oxidation. The organic components of the waste are converted to carbon dioxide and water with potential recovery of the heating value; inorganic components are separated out as solid salts, which can be reused or discarded safely; water in aqueous waste is recovered in a highly purified form, which can be reused without further treatment. The wastes are treated in an enclosed system so that escape of pollutants to the environment is eliminated. Furthermore, there is a minimal number of processing steps so that the capital investment compares very favorably with alternative processes. The most significant feature of this new approach is that it can be cost-effective. When the organic content of the waste,is 5% or more, the process is capable of generating sufficient net power to cover the entire cost of waste treatment.

INTRODUCTION

The MODAR process is based, in part, on a discovery made in 1975 by Modell and co-workers at M.I.T. In the course of investigating the effects of treating aqueous solutions of organics at high temperatures and pressures, it was found that complex organic substances can be dissolved and broken down into low molecular weight products when treated under conditions where water is supercritical (i.e., above 374°C and 218 atm). The discovery is the basis of U.S. Patent No. 4,113,446 [Modell, *et al*. (7)], originally assigned to M.I.T. and now exclusively licensed to MODAR.

In 1979, Modell carried this work one step further. He proposed a new method of destroying wastes by dissolving both organic material and oxygen in supercritical water (SCW), and then carrying out the oxidation in the supercritical water medium. MODAR was formed in 1980 to develop and commercialize this new SCW oxidation process. The SCW oxidation process has been reduced to practice with outstanding technical results. In addition, preliminary economic analyses indicate that the process is potentially much less expensive in both capital and operating costs when compared to high temperature incineration.

TECHNICAL CONCEPTS

In the supercritical region, water exhibits properties that are far different from normal liquid water [see, e.g., Franck (3)]. The density of supercritical water (0.05-0.5 g/cm^3) is low enough and the temperature high enough to essentially eliminate hydrogen bonding [Franck (4)]. As a result, the dielectric constant is diminished to about 3 to 10 and water becomes an excellent solvent for organic substances [Connolly (2)]. At somewhat higher temperatures (above 500°C), the density of water is reduced to 0.05 - 0.1 g/cm^3 and the dielectric constant is less than 2. Under these conditions, inorganic salts become only sparingly soluble [Martynova (6)]. Salts such as NaCl act as weak electrolytes with little, if any, dissociation into ions [Marshall (5)]. Thus, the solubility characteristics of supercritical water are the inverse of those of normal liquid water.

Above 350°C, water reacts with organic materials in a way that leads to the formation of low molecular weight products [Amin (1)]. Whereas many organic compounds tend to form a high molecular weight char at temperatures below 350°C, at supercritical conditions the same organics are reformed to gases (e.g., CO, H_2, CH_4, CO_2) and volatile organic liquids (alcohols, aldehydes, furans) without producing any char.

The products of SCW reforming can be subjected to oxidation while still under supercritical conditions. It is well-known that aqueous solutions of organics will undergo oxidation at temperatures of 200 to 300°C. This phenomenon is the basis of the conventional wet oxidation or Zimpro process, which is operated under subcritical conditions [see, e.g., Wilhelmi and Knopp (8)]. The wet oxidation process requires residence times of 20 minutes to 1 hour to achieve destruction efficiencies which are, at best, mediocre (70 to 95% reduction in total organic carbon). On the other hand, under supercritical conditions, the residence time required for oxidation is less than 1 min, which greatly reduces the volume of the oxidizer vessel. In addition, oxygen is completely miscible with supercritical water, and the oxidation can be conducted under homogeneous (i.e., single phase) conditions. Thus, oxidation under SCW conditions is an efficient means of ultimate disposal of organics.

When toxic or hazardous organic chemicals are subjected to SCW oxidation, carbon is converted to CO_2 and hydrogen to H_2O. The chlorine atoms from chlorinated organics are liberated as chloride ions. Similarly, nitro-compounds can be converted to nitrates, sulfur to sulfates, phosphorus to phosphates, etc. In other words, hetero-atoms form oxy-acid anions. Upon addition of appropriate cations (e.g., Na^+, Mg^{++}, Ca^{++}), inorganic salts can be formed.

Finally, when the concentration of organics is above 5 wt%, the heat of oxidation is sufficient to bring the supercritical stream to temperatures in excess of 550°C. At these conditions, inorganic salts have extremely low solubilities in water. Inorganic salts will be precipitated out and readily separated from the aqueous phase. After removal of inorganics, the resulting aqueous phase is a highly purified stream of water at high temperature (>500°C) and high pressure (3700 psia). It can be used as a source of high-temperature process heat or fed to conventional supercritical steam turbines for generating power.

PROCESS DESCRIPTION

The MODAR system for hazardous waste destruction makes use of water in its supercritical state (SCW) as the process medium for carrying out the destruction of organic materials by oxidation. Key to the success of the process is the fact that organic substances and gases, including oxygen, are completely soluble in SCW, whereas inorganic salts exhibit greatly reduced solubilities under process conditions. Thus, it becomes conceptually possible to carry out "combustion" reactions by dissolving organic substances and oxygen in SCW, bringing them into intimate contact in a single-phase medium. The temperatures and molecular densities allow the conventional oxidation reactions to proceed rapidly and essentially to completion. In fact, one might expect these conditions to be more favorable for carrying combustion reactions to completion than those of conventional incineration processes, where volatilization and mass transport of reaction species are limiting factors. Furthermore, the reduced solubility of salts makes possible the direct removal of undesirable reaction products through precipitation.

A schematic flowsheet for the MODAR process described above is given in Fig. 1. The process consists of the following steps:

(1) The toxic or hazardous waste is slurried with make-up water to provide a mixture of about 5 to 10 wt% organics. The slurry is pressurized and heated to supercritical conditions to avoid char formation. Heating is attained by mixing the feed with superheated SCW, which is generated in a subsequent step. During a short residence time in the tube leading to the oxidizer, organics in the feed are converted to combustible gases, low to intermediate molecular weight compounds (furans, furfurals, alcohols, aldehydes) and inorganic salts.

(2) Air or oxygen is pressurized and mixed with the feed. Since the water is still supercritical, the oxidant is completely miscible with the solution (i.e., the mixture is a single, homogeneous phase). Organics are oxidized in a controlled but rapid reaction. Since the oxidizer operates adiabatically, the heat released by combustion of readily oxidized components is sufficient to raise the fluid phase to temperatures where all organics are oxidized rapidly. For a feed of 5 wt% organics, the heat of combustion is sufficient to raise the oxidizer effluent to at least 550°C.

(3) The effluent from the oxidizer is fed to a salt separator, where inorganics originally present in the feed are removed as a solid slurry. At 500°C and above, the solubility of inorganics in SCW is extremely low.

(4) A portion of the superheated SCW is recycled to an eductor upstream of the SCW oxidizer. This operation provides for sufficient heating of the feed to bring the oxidizer influent to supercritical conditions.

(5) The remainder of the superheated SCW (with some CO_2 and N_2) is available for power generation or use as high-pressure steam. A portion of the available energy is used to generate the power required to pressurize feed and oxidant. Note that the energy required to pressurize the oxidant is recovered in the expansion of the products of combustion in the superheated SCW turbine. Thus, the method of oxidation is analogous to that of a gas turbine.

As a waste destruction process, the MODAR concept has several advantages over conventional processes. The chemical reactions which occur are carried out in a closed system, making it possible to maintain total physical control of waste materials from storage, through the oxidation process, to the eventual discharge of the products of combustion and any associated wastes. This feature provides positive assurance of environmental protection. In addition, bench-scale results indicate essentially complete destruction of chemically stable materials (such as PCB's) at projected costs which are well within those presently associated with hazardous waste operations. Finally, the process can be adapted to a wide range of feed mixtures and scales of operation. Skid-mounted, transportable systems are being designed as well as larger-scale stationary units.

EXPERIMENTAL

Under the joint sponsorship of the U.S. Army Medical Bioengineering Research and Development Laboratory (USABMERL) and EPA's Office of Research and Development, MODAR conducted a series of experiments to demonstrate the technical feasibility of the SCW oxidation process. A

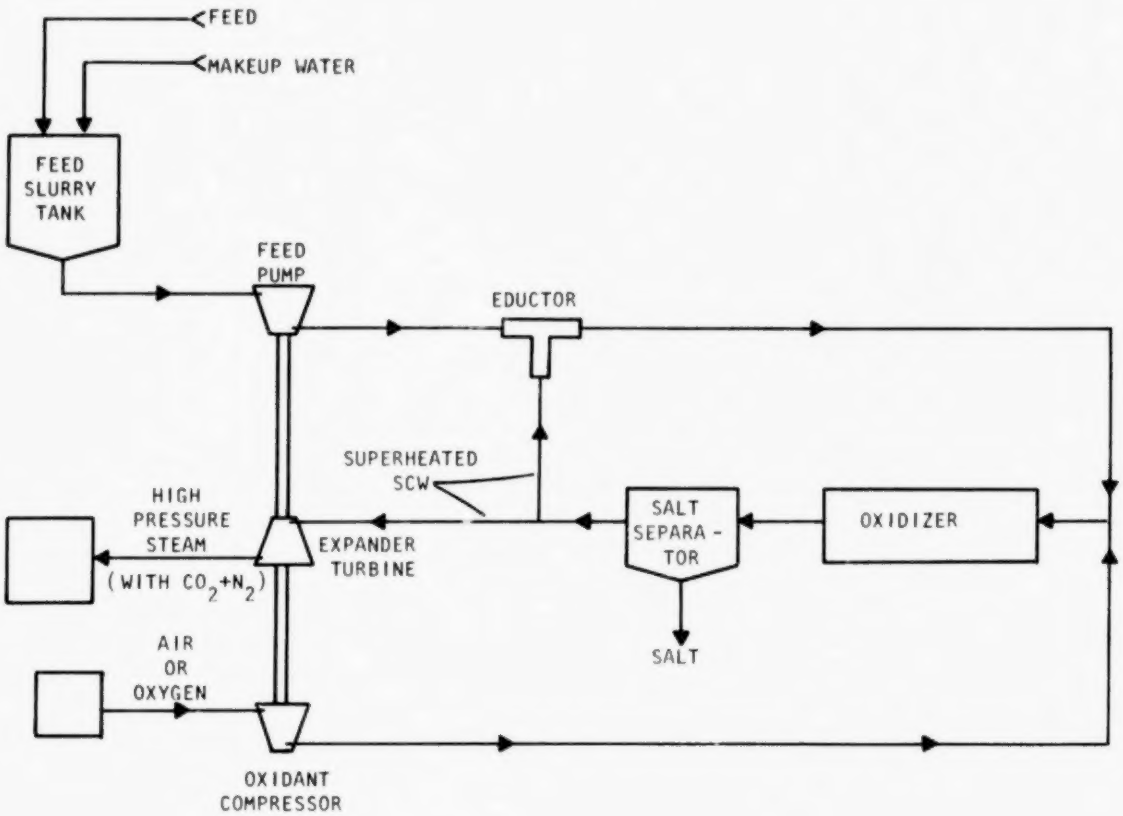


FIGURE 1. SCHEMATIC OF THE MODAR SCW OXIDATION PROCESS

continuous flow bench-scale system with an organic throughput of 1 gallon per day was used for these tests. The reactor was constructed from Hastelloy C-276, with an i.d. of 0.88 in. and a length of 2 ft. The reactor effluent was cooled to room temperature and depressurized to 1 atm. Liquid effluents were analyzed for total organic carbon (TOC), pH, and by ion-selective electrodes and gas chromatography/mass spectrometry (GC/MS). Gaseous effluents were analyzed by gas chromatography (GC) for low molecular weight hydrocarbons and permanent gases. The terminology used to describe the results is given in Table 1.

Since the GC/MS analysis of liquid effluents is of particular importance, some details will be described. Liquid effluent samples were first extracted with dichloromethane and then concentrated in a Kuderna-Danish apparatus. One microliter of this solution was injected into a stand-alone gas chromatograph and an appropriate aliquot (1-2 ul, dependent on the concentration of the solution as judged from the GC experiment) injected into the GC/MS system. A Varian 3700 gas chromatograph, equipped with flame ionization detector and automatic integrator, was used for stand-alone GC analysis. Columns were 15 m fused quartz coated with either SE-30 or SE-52. Another Varian 3700 gas chromatograph was coupled to a Varian-mat 212 double focusing mass spectrometer via an open-split interface. The conditions on the gas chromatograph were the same as on the corresponding stand-alone GC run. The mass spectrometer was scanned from M/Z of 30 through 500 at cycle times ranging from 2.0-2.8 seconds. The resolution of the mass spectrometer was set to 1:1000. The GC/MS was interfaced to a Varian-mat SS-200 data system. This computer contains all the mass spectrometry data processing and evaluation programs developed at M.I.T. over the years. The data were searched for compounds of interest either by inspection of the mass spectra at GC-peaks in the proper retention areas or by plotting mass chromatograms of the characteristic masses of the compounds (e.g., M/Z of 154, 188, 222, 256, 290, 324, 358, 392 and 426 for biphenyl through octachlorobiphenyl), followed by inspection of the mass spectra at these maxima.

Alternatively, selected mass spectra were compared with the NIH/EPA/MSDC mass spectral library or automatically microfilmed for easier visual inspection.

As a search for tetrachlorodioxins and tetrachlorodibenzofurans, the mass chromatograms of M/Z 320 and 304, respectively, were plotted and the mass spectra at any maximum in the plot were inspected for the characteristic M/Z 320, 322, 324, 326, 328 pattern (304, 306, 308, 310, 312 for TCDF). If found, the entire spectrum would be compared to the authentic spectra.

After identification of the components of interest, their concentrations were estimated from the stand-alone GC trace. Peak heights were determined and converted to nanograms using known amounts of naphthalene, methyl naphthalene and phenanthrene for the estimation of aromatics and the phthalates, and 4,4'-dichlorobiphenyl for the PCB's and other aromatic chlorinated compounds.

RESULTS AND DISCUSSION

MODAR has conducted an extensive series of bench-scale tests to establish the technical feasibility of SCW oxidation. A typical series of tests with organic chloride feeds is described herein.

The feed materials and compositions for each run in this series are given in Table 2. Chronologically, we began this series with a model compound, DDT, and progressed to more complex mixtures.

A summary of the results for this series is given in Table 3. Note that the compounds identified by GC/MS analysis are identified by letters at the bottom of Table 3; the structures are given in Table 4. Using the methods described in the prior section, the mass spectra were searched for each of the compounds shown in Table 4; only those found in one experiment or another are

TABLE 1. DEFINITION OF TERMS

Residence Time = Volume of reactor divided by volumetric flow rate of process fluid.

Organic Carbon In (ppm) = Carbon content of organic/water feed mixture as it enters the reactor.

Organic Carbon Out (ppm) = Total carbon in liquid effluent after sparging or total carbon minus inorganic carbon.

Destruction Efficiency = $\frac{\text{(Organic Carbon In - Organic Carbon Out)}}{\text{Organic Carbon In}} \times 100$

Combustion Efficiency = $[CO_2/(CO_2 + CO + CH_4)] \times 100$ concentrations in the effluent vapor, as measured by GC analysis.

Organic Chloride In (ppm) = Chloride content of organic/water feed mixture, as it enters the reactor.

Organic Chloride Out (ppm) = Residual organic chloride as determined by GC/MS.

Organic Chloride Conversion = $\frac{\text{(Organic Chloride In - Organic Chloride Out)}}{\text{Organic Chloride In}} \times 100$

TABLE 2. COMPOSITION OF FEED MIXTURES FOR RUNS 11 - 15

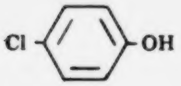
		wt %	wt % Cl
Run 11			
DDT	$C_{14}H_9Cl_5$	4.32	2.133
MEK	C_4H_8O	95.68	-
		100.0	2.133
Run 12			
1,1,1-trichloroethane	$C_2H_3Cl_3$	1.01	0.806
1,2-ethylene dichloride	$C_2H_2Cl_2$	1.01	0.739
1,1,2,2-tetrachlorethylene	C_2Cl_4	1.01	0.866
o-chlorotoluene	C_7H_7Cl	1.01	0.282
1,2,4-trichlorobenzene	$C_6H_3Cl_3$	1.01	0.591
biphenyl	$C_{12}H_{10}$	1.01	-
o-xylene	C_8H_{10}	5.44	-
MEK	C_4H_8O	88.48	-
		100.0	3.284
Run 13			
hexachlorocyclohexane	$C_6H_6Cl_6$	0.69	0.497
DDT	$C_{14}H_9Cl_5$	1.00	0.493
4,4'-dichlorobiphenyl	$C_{12}H_8Cl$	1.57	0.495
hexachlorocyclopentadiene	C_5Cl_6	0.65	0.505
MEK	C_4H_8O	96.09	-
		100.0	1.99
Run 14			
PCB 1242	$C_{12}H_XCl_{4-6}$	0.34	0.14
PCB 1254	$C_{12}H_XCl_{5-8}$	2.41	1.30
transformer oil	$C_{10}-C_{14}$	29.26	-
MEK	C_4H_8O	67.99	-
		100.0	1.44
Run 15			
4,4'-dichlorobiphenyl	$C_{12}H_8Cl$	3.02	.96
MEK	C_4H_8O	96.98	-
		100.0	0.96

TABLE 3. SUMMARY OF RESULTS: OXIDATION OF ORGANIC CHLORIDES

Run No.	11	12	13	14	15
Residence Time (min)	1.1	1.1	1.1	1.1	1.3
Carbon Analysis					
Organic Carbon In (ppm)	26,700.	25,700.	24,500.	38,500.	33,400.
Organic Carbon Out (ppm)	2.0	1.0	6.4	3.5	9.4
Destruction Efficiency (%)	99.993	99.996	99.975	99.991	99.97
Combustion Efficiency (%)	100.	100.	100.	100.	100.
Gas Composition					
O_2	25.58	32.84	37.10	10.55	19.00
CO_2	59.02	51.03	46.86	70.89	70.20
CH_4	-	-	-	-	-
H_2	-	-	-	-	-
CO	-	-	-	-	-
Chloride Analysis					
Organic Chloride In (ppm)	876.	1266.	748.	775.	481.
Organic Chloride Out (ppm)	.023	.037	<.028	.032	.036
Organic Chloride Conversion (%)	99.997	99.997	99.996	99.996	99.993
GC/MS Effluent Analysis					
Compound B (ppb Cl)	-	-	-	-	-
C	-	-	-	-	-
E	-	9	-	14	-
F	18	12	18.	-	-
H	-	-	<4.	-	-
K	5	16	<5.	6	-
M	-	-	0.2	-	-
N	-	-	0.3	-	36
O	-	-	-	12	-

TABLE 4. COMPOUNDS SEARCHED BY GC/MS ANALYSIS

A:



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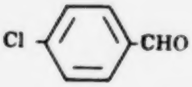

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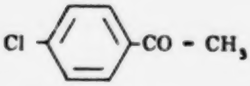

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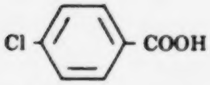

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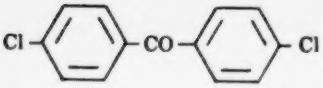

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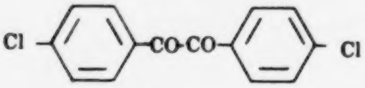

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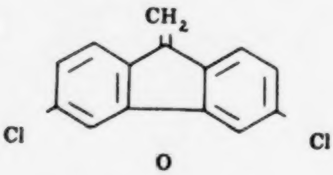

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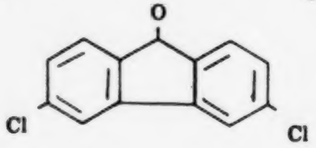

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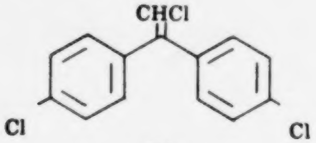

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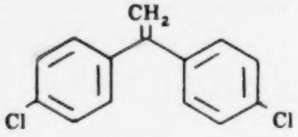
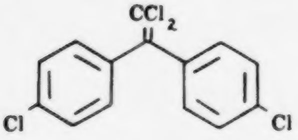
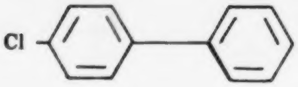


K:



L: Isomer of I.

M:



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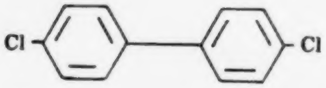
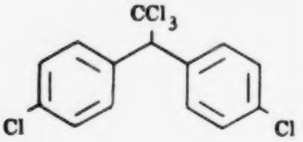
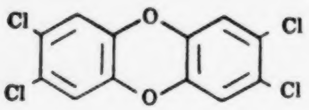


O:



P:



Notes: p-Isomers are assumed, based on the position of the chlorine atoms in the starting materials.

Compound F - No authentic MS

Compound G - No MS available in literature given in Table 3. In other words, compounds A,D,G,I,J,L and P were not present in the test results shown in Table 3. It should be especially noted that chlorinated dibenzo-p-dioxins were never found in any of our effluents, even though the mass spectra were specifically searched for them.

The results of run 11, as shown in Table 3, are representative of one of our most important findings: organic chlorides can be destroyed by SCW oxidation with efficiencies above 99.99%. In run 11, both carbon destruction efficiency and organic chloride conversion exceed 99.99%.

The feed for run 12 consisted of a mixture of five organic chlorides (see Table 2), two of which were aromatic chlorides (o-chlorotoluene and 1,2,4-trichlorobenzene). Once again, the carbon destruction efficiency exceeded 99.99%. The organic chloride conversion is 99.997%.

It should be noted that chlorinated compound K, which is DDE (see Table 4), was found in the liquid effluent of run 12, although the concentration was minute (16 ppb). It is extremely difficult to accept the hypothesis that the DDE was formed by reaction or rearrangement of any of the chlorinated organics in the run 12 feed. We are more apt to believe that we had cross-contamination of samples from the low pressure, room temperature portion of our bench scale system. To prevent cross-contamination, an acetone wash system was later installed.

The feed for run 13 was a mixture of four non-volatile chlorinated organics, including hexachlorocyclohexane (Lindane) and 4,4'-dichlorobiphenyl (a model PCB compound), both of which should be relatively stable. As shown in Table 3, the carbon destruction and chlorine conversion efficiencies were very good, the latter being somewhat higher than the former.

The feed for run 14 was a mixture of spent transfomer oil, containing two PCB's, which was diluted with MEK. Once again, both carbon destruction and chlorine conversion exceeded 99.99%. Note that the residual organic chlorides identified by GC/MS (compounds E,K and O) are all DDT-related species. Thus, those trace quantities are probably cross-contaminants from run 13. It should also be noted that for run 14, mass spectra were searched for all chlorinated biphenyls. That is, we specifically looked for trace quantities of tri-, tetra-, penta- and hexa-chlorobiphenyl, in addition to the mono- and di-chloro species (compounds M and N in Table 4). At the detection limit of < 10 ppb, none of these chlorinated biphenyls were found. If we discount compounds E,K and O as cross-contaminants, then the chlorinated biphenyl conversion efficiency is >99.9994%.

Run 15 was an experiment with a model PCB, 4,4'-dichlorobiphenyl. The results obtained in run 15 were once again excellent.

CONCLUSION

The present results indicate that SCW oxidation gives essentially complete destruction of refractory organic compounds in residence times on the order of 1 min. As shown in Table 5, a broad spectrum of organic materials have been tested; the results are similar to those described above. In general, the SCW oxidation is non-specific.

Although not demonstrated here, the process has other advantages which make it an excellent means of hazardous as well as non-hazardous waste disposal. Auxiliary pollution control equipment for effluent streams is unnecessary. The process is applicable to wastes in the form of liquids, solids, or sludges. It is particularly applicable to aqueous waste streams containing mixtures of organic and inorganic materials, with inorganics being recovered as a solid. Upon removal of inorganic compounds, the high temperature, high pressure mixture of steam and gases is available to be used as process heat or for generation of power. When the organic content of the waste is greater than 5%, sufficient net power may be generated to cover the entire cost of treatment. The process cost compares very favorably with alternative schemes, and is expected to see wide application in the near future.

TABLE 5. MATERIALS TESTED UNDER SCW OXIDATION

Dextrose
Cyclohexane
Biphenyl
Benzene
1,1,1-Trichloroethane
1,2-Ethylene Dichloride
o-Chlorotoluene
1,2,4-Trichlorobenzene
o-Xylene
Hexachlorocyclohexane
4,4'-Dichlorobiphenyl
Hexachlorocyclopentadiene
DDT
PCB 1234
PCB 1254
2,4-Dinitrotoluene
Urea
Methyl ethyl ketone

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THE DESTRUCTION OF VARIOUS ORGANIC SUBSTANCES BY A CATALYZED WET OXIDATION PROCESS

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ABSTRACT

Research was initiated to determine the ability of the catalyzed wet oxidation process to destroy organic substances that are representative of materials found in hazardous wastes. Catalyzed wet oxidation uses homogenous catalysts in conventional chemical reaction equipment to ultimately oxidize an organic substance to carbon dioxide. Fifteen organic compounds were studied in a laboratory-scale batch reaction system. These compounds were destroyed with reaction conditions ranging from 165°C to 275°C, 150 psig to 1000 psig and reaction time from 5 minutes to 420 minutes. Preliminary designs using a portable 1000 gallon treatment process have been made based on demonstrated destruction rates. The cost of treating some organics range from $0.12/lb of organic to $1.04/lb of organic.

INTRODUCTION

The United States is facing a major environmental problem as it becomes more aware of the production and handling of toxic and hazardous wastes. These wastes have been produced for many years, but their disposal has not been controlled. The recent increase in public awareness and concern has prompted the United States Environmental Protection Agency (USEPA) to evaluate technologies aimed at solving the problem. Of particular interest is the development and application of new technologies to the problems associated with abandoned chemical waste disposal sites such as Love Canal and the Valley of the Drums. The estimate of the number of such sites in the United States and the cost to clean them up is staggering. Treatment of the leachate and ground waters and ultimate disposal of the sludges, soils, liquids, solids, and containers in the site are typical disposal problems.

The most desirable technology for dealing with the problem of chemical disposal sites is a process that 1) achieves complete destruction of toxic and hazardous chemicals and minimizes by-products and chemical remnants requiring disposal; 2) minimizes the energy required for disposal, especially supplemental fuels; 3) has few unit operations; 4) has low chemical usage; 5) has low volume effluents, so that polishing treatment to achieve total containment can be readily implemented; 6) is easily pilot-planted; and 7) is transportable to the landfill sites.

The present study evaluates a new catalytic wet oxidation technology for the treatment of toxic and hazardous materials. It is applicable to both aqueous wastes and organic residues. Earlier work resulted in U.S. Patent 3,984,311 (1) and two additional patent applications that describe catalyst systems for destruction of various chemicals. The data show fast destruction rates for compounds such as nitrated and chlorinated phenols, 2,4-D, aklylphosphorothioates, and short chain fatty acids. On the basis of this earlier range-finding testing and economic evaluation, the technology appears to have wide-ranging applicability and potential for alleviating significant waste disposal problems facing the

United States. The data on which this paper was developed was supported by funds from the USEPA.

CATALYZED WET OXIDATION PROCESS CONCEPT

The catalyzed wet oxidation process is based on U.S. Patent 3,984,311, originally assigned to The Dow Chemical Company with right, title, and interest now owned by IT Enviroscience for development and commercialization. The patent teaches the use of a co-catalyst system consisting of bromide and nitrate anions in an acidic, aqueous solution. Continued research with the co-catalyst system has led to the development of a new catalyst mixture which is more effective for oxidizing insoluble organics. The new catalyst system consists of bromide, nitrate, and manganese ions in acidic solution. A patent for the new catalyst has been allowed (U.S. 4,276,198) and assigned to IT Enviroscience (2). The destruction of most organics by these catalyst systems is rapid and essentially complete.

The keys to the operation of this catalyst system are the mechanism of oxygen fixation and the fact that it is a water-soluble, single-phase catalyst system--a homogeneous catalyst as contrasted to a heterogeneous catalyst. In conventional wet oxidation, heat and pressure are used to drive the dissolution of oxygen from air and the reaction with dissolved organics in aqueous solution. In the bromide-nitrate based catalyst systems the transfer of oxygen to the dissolved state is speeded up by using very rapid gas and liquid reactions associated with the catalyst components. The importance of the enhanced oxygen transfer is the ability to oxidize organics at much lower temperatures than uncatalyzed wet oxidation, 165-200°C versus 250-325°C. The lower operating temperatures also mean lower operating pressures which not only reduces capital cost but operational problems.

The second important aspect of the catalyst system is its homogeneous nature which permits application to the destruction of toxic or hazardous organic residues, such as still bottoms or other organic wastes. The advantages of a homogeneous catalyst are best utilized by using a reactor design which is different from conventional wet oxidation processes. In simplest form the reactor, a continuously stirred tank reactor (CSTR) contains the catalyst solution. Air and the waste are continuously pumped into the reactor and the organics are oxidized with the heat of reaction driving off water. The only materials to leave the reactor are CO_2, N_2, water vapor, any volatile organics and inorganic solids formed. Water is condensed and returned to the reactor, if necessary, as are condensable organics. Any inorganic salts or acids which may be formed have to be removed by treatment of a closed loop stream of catalyst solution. Such treatment is individually designed utilizing conventional technologies, such as filtration or distillation. The vent gases from the reactor are low in volume and may, if necessary, be treated by conventional techniques, such as absorption, adsorption, or scrubbing. The most important features of this process concept are that non-volatile organics remain in the reactor until destroyed, and that there is no aqueous bottoms product.

COMPOUND SELECTION

The study of a process associated with chemical wastes needs to evaluate a wide range of chemical compounds to evaluate the applicability of the process. In order to meet this requirement fifteen compounds were selected from various chemical groupings of the EPA priority pollutant list. The specific compounds chosen from each grouping were made based on the likelihood of finding the chemical in industrial waste and chemical disposal sites. In certain cases a lower toxicity compound was substituted for a highly toxic compound, e.g., diphenyl hydrazine substituted for benzidine, when it presented an unacceptably high risk to laboratory personnel. The chemical groups and the compounds studied were:

- Halogenated hydrocarbons
  - Ethylene dibromide
  - Hexachlorobutadiene
  - Trichloropropane
- Pesticides
  - Atrazine
  - DDT
  - Malathion
  - Mirex
- Phenols
  - Pentachlorophenol
- Phthalates

    - Di-n-butyl phthalate
- Polynuclear aromatics
    - Chloroanthracene
- Nitrogen containing compounds
    - Acetonitrile
    - Chloroaniline
    - Diphenyl hydrazine
    - Nitrobenzene
- Aromatic
    - o-Xylene

EXPERIMENTAL METHOD

The experimental evaluation of catalyzed wet oxidation was conducted in a 1-liter agitated titanium autoclave. The destruction rate of the compounds was measured at various operating conditions with batch reactions. Typical operating conditions were 165-250°C, 0.5% Br^-, 5.0% NO_3^-, 0.25% Mn^{+2}, 30-120 minutes reaction time, and 20% excess oxygen over stoichiometric. The procedure for conducting the oxidation reactions consisted of loading the reactor with the desired quantity of deionized water, HBr, and organic to be oxidized. The reactor was sealed, purged with oxygen, and pressurized with sufficient oxygen to totally oxidize the organic. The reactor was then heated to the desired operating temperature and the remaining catalysts, HNO_3, and $MnSO_4$, were added to the reactor with oxygen pressure. The reaction was run for the desired time period. At the termination of the reaction, the reactor was cooled to room temperature with cooling water. The pressure was then vented and any free bromine was reduced to bromide by the addition of 10 ml of sodium bisulfite solution to prevent operator exposure to toxic bromine vapors. The reactor was opened and the aqueous contents were aspirated from the reactor. All internal surfaces of the reactor were rinsed twice with solvent, methylene chloride. The solvent rinsings were aspirated from the reactor and combined with the aqueous effluent. The aqueous phase was extracted with the solvent rinse and two successive 50-ml portions of solvent to recover unreacted organics and reaction by-products. The combined solvent extracts were analyzed by gas chromatography and gas chromatography/mass spectrometry (GC/MS). The destruction rate of the organic was also measured by the formation of CO_2, by gas chromatography, and the formation of Cl^- (from chlorinated organics), by ion chromatography. All of these methods followed quality assurance/quality control (QA/QC) procedures as outlined in the *IT Enviroscience Analytical Chemistry Control Manual*. These measurements were used to determine the completeness of the organic destruction.

EXPERIMENTAL RESULTS

Summary

For the purpose of evaluating the applicability of the process to treat hazardous wastes in chemical landfills, the results of the individual compound studies are grouped into two major categories, fast and slow destruction rate compounds. The definition of fast and slow destruction rates can be set at any level, but the results of the compounds studied can be split as follows. Compounds that were destroyed at low temperatures, less than 200°C, and short reaction times, less than 60 minutes, were classified as fast destruction rate compounds. This group includes atrazine, butyl phthalate, chloroaniline, diphenyl hydrazine, ethylene dibromide, malathion, and pentachlorophenol. Compounds in the other group (slow destruction rate) were more difficult to destroy. These compounds required higher reaction temperatures, up to 250°C, and longer reaction times. This group includes the other compounds studied, acetonitrile, chloroanthracene, DDT, hexachlorobutadiene, mirex, nitrobenzene, trichloropropane, and o-xylene.

Atrazine

The destruction rate for atrazine was very fast, apparently due to both the instability of the heterocyclic nitrogen ring at high temperatures and the oxidation by the catalysts. The instability of the atrazine molecule was observed in the first experiment without catalysts. At a temperature of 163°C, 51.5% of the atrazine was oxidized with release of a comparable amount of chloride (58.3%) but very little CO_2 formation. This corresponding release of Cl^- with atrazine decrease suggests an initial C-Cl bond rupture. Whether this reaction occurs in the presence of the catalyst system is unknown and beyond the scope of this investigation. However, the addition of the Br-NO_3-Mn catalysts increased the oxidation of atrazine (99.9%) and the formation of CO_2 (45.3%) and chloride (83.1%). A later experiment using only bromide and nitrate catalysts had a similar oxidation rate for atrazine (99.9%) and a formation rate of chloride (100%) but very little formation of CO_2 (0.6%), indicating the manganese plays a critical role in the complete oxidation of atrazine to carbon dioxide. Because of the demonstrated importance of manganese in the catalyst system, the remaining experiments were all performed with the three-catalyst system, Br-NO_3-Mn. The experimental variables of reaction time, temperature, and atrazine concentration were further evaluated to determine the maximum destruction rate for the catalytic oxidation of atrazine.

The rapid oxidation rate of atrazine and the limited accuracy of the CO_2 and chloride analysis made it difficult to evaluate optimum oxidation conditions. However, the experimental data can be examined for trends toward optimum reaction parameters. Increasing the reaction temperatures from 165 to 200°C increased the complete destruction rate to CO_2 by approximately 40%, during a 30 minute reaction. The effect of time during these experiments was minimal, with less than an 18% increase in formation of CO_2 with a four-fold increase in reaction time, from 30 to 120 minutes. The effect of atrazine concentration was determined by increasing its concentration ten-fold from 0.1% to 1.0%. The destruction rate measured by the oxidation of atrazine and the formation of CO_2 remained constant, indicating a first-order kinetic relationsip for atrazine concentrations. The first-order relationship of concentration, coupled with the fast oxidation rate, permits the design of a treatment process that can destroy large quantities of atrazine in relatively small equipment. Therefore, a waste treatment process with small equipment (low capital cost) and high throughput (via high destruction rates) would be a very economical process to install and operate. A catalyzed wet oxidation process offers a technically and economically viable alternative for destroying atrazine or similarly structured compounds.

Butyl Phthalate

The oxidation of butyl phthalate was different from the behavior exhibited by atrazine. Butyl phthalate showed considerable resistance to wet oxidation without the presence of catalysts. At 164°C only 6% of the initial butyl phthalate was oxidized in 30 minutes with 1.2% of the initial amount being completely oxidized to CO_2. The addition of the Br-NO_3-Mn catalyst increased the oxidation rate of butyl phthalate to 86.6% in 30 minutes at 163°C with 50.6% of the initial material being totally oxidized to CO_2. The effect of the increased reaction time increases both the oxidation of the butyl phthalate and the formation of CO_2. A four-fold increase in time, 30 to 120 minutes, increased the oxidation rate by 13%. This small effect on reaction time indicates that the oxidation of butyl phthalate probably follows a multistep process and that although the initial steps are fast, the final oxidation reactions are slow. Based on earlier catalyzed oxidation experiments with carboxylic acids, e.g., acetic acid, it is postulated that the early oxidation reactions yield relatively stable by-products which oxidize at a much slower rate.

The disappearance of butyl phthalate is first-order, with similar oxidation rates, 96.0% vs. 97.6% for 0.1% and 1.0% butyl phthalate experiments. This result is consistent with early studies of water-soluble organics and the data from the study of atrazine. The effect of various catalyst mixtures on the oxidation rate of butyl phthalate and the formation rate of CO_2 was similar to the results reported for atrazine. Although the actual effects of the catalysts are small, the trends are similar. The removal of manganese from the mixture decreases the oxidation rate of butyl phthalate and the formation of CO_2. Increasing either the bromide or nitrate concentration slightly increases the oxidation rate of butyl phthalate but has little effect on the formation of CO_2.

Analysis of selected experiments by GC/MS revealed that the extractable by-products from the oxidation of butyl phthalate fall into two categories, brominated organics and phthalic acid. Brominated by-products, bromoform and dibromopropane, were present in the solvent extracts of all the samples analyzed by GC/MS. Phthalic acid was identified in the extracts of two later experiments, both high butyl phthalate concentration experiments.

Chloroaniline

The oxidation of chloroaniline was similar to the oxidation of atrazine in that chloroaniline was partially oxidized with no catalyst present. Two experiments were conducted with no catalyst at temperatures of 165 and 199°C. It is not known whether the uncatalyzed reaction was due to a wet oxidation reaction or to a rearrangement reaction. However, the ease of oxidizing chloroaniline without catalysts usually results, as in the case with atrazine, in rapid and essentially complete oxidation with the Br-NO_3-Mn catalyst system. The solvent-extracted effluent from the third experiment was analyzed by GC/MS for reaction by-products. The compounds identified were small amounts of dibromochloromethane, bromoform, tetrabromoethane, and various brominated chlorobenzenes. These by-products are consistent with other analyses of reactor effluents. The by-products or partially oxidized compounds are ultimately oxidized to CO_2, HCl, and H_2O.

Chloroanthracene

The oxidation of chloroanthracene was very different from any of the earlier compounds studied. The initial experiment with no catalysts showed very little oxidation. However, the rest of the experiments showed very high destruction rates by disappearance of chloroanthracene and by the limited formation of CO_2 and Cl^-. Analysis of the reactor effluent by gas chromatography showed the presence of a major reaction by-product, which was identified by GC/MS as chloroanthracenedione with smaller amount of bromoform, tetrabromoethane, and dibromochlorobenzene. The significance of the chloroanthracenedione by-product is that it is the first major by-product identified which was not brominated. Later experiments show that chloroanthracenedione is oxidized further at longer reaction times or under more stringent conditions. The similar destruction rates as measured by CO_2 and Cl^- formation indicate that the chloroanthracenedione can be completely oxidized.

Ethylene Dibromide

The oxidation of ethylene dibromide (EDB) follows a multistep sequence that initially results in the disappearance of EDB with very little CO_2 formation. This occurred in the first and third experiments when no catalysts were used at a reactor temperature of 164°C. The mechanism which causes this reaction is not known, but the addition of the Br-NO_3-Mn catalyst to the reactor results in the oxidation of the organics to CO_2. The excess formation of CO_2 is attributed to an analytical error associated with the CO_2 analysis rather than to the complete oxidation of all the EDB placed in the reactor. The only identified by-product of the oxidation reaction was bromoform in the second experiment.

Hexachlorobutadiene

The oxidation of hexachlorobutadiene was more difficult than for any of the compounds tested earlier. Wet oxidation at 165°C without catalysts was ineffective in destroying hexachlorobutadiene. Even the addition of the Br-NO_3-Mn catalyst did not improve the oxidation rate at 165°C. The resistance of hexachlorobutadiene to oxidation required a higher reaction temperature and a longer reaction time to achieve destruction. After two hours at 250°C, 25% of the hexachlorobutadiene was oxidized to CO_2 and Cl^-. Although this destruction rate is relatively slow, the catalyst system successfully destroyed hexachlorobutadiene. Further experiments with longer reaction times increased the destruction rate but the overall rate, 45% destruction in 7 hours, was still too slow to effectively destroy large quantities of hexachlorobutadiene. However, experiments with higher concentrations of hexachlorobutadiene yielded much higher destruction rates. A later experiment had the greatest destruction of hexachlorobutadiene, 91% in 2 hours at 242°C. It is unknown whether the high destruction rate was due to the presence of greater quantities of chloride or to an insoluble organic phase. The reason for the improved destruction rate could be the subject of future laboratory studies. Analysis of the reactor effluent from the hexachlorobutadiene experiments by GC/MS revealed the presence of hexachloroethane, an impurity of hexachlorobutadiene, and bromoform, a by-product of the oxidation.

Malathion

Malathion was so unstable at temperatures higher than 165°C that none could be detected in the reactor effluent. The effect of temperatures was isolated by running an uncatalyzed oxidation at room temperature. Greater than 91% of the malathion was recovered from the reactor. This experiment demonstrated that malathion is thermally unstable. The only significant experimental difference observed was that uncatalyzed oxidation gave limited CO_2, indicating only partial oxidation of malathion.

In the presence of the catalyst, malathion was oxidized completely to CO_2. The high CO_2 formation results, 105% to 113%, indicate complete oxidation. A few trace organics were identified in the reactor effluent by GC/MS. These were methylene bromide and bromoform, which could be final remnants from the oxidation of malathion.

Mirex

Of the fifteen organics studies, mirex was the most resistant to oxidation. The first experiment, no catalysts, showed no oxidation of mirex and greater than 99% recovery at 199°C. The addition of the standard Br-NO_3-Mn mixture only increased the oxidation rate to 8.5% in 65 minutes. With the apparent high resistance to oxidation later experiments utilized much higher reaction temperatures to attempt mirex oxidation. At temperatures as high as 274°C, only 15.9% of the mirex could be oxidized. No extra compounds were indicated by analysis of the reactor effluent, so no analyses by GC/MS were performed.

Nitrobenzene

Nitrobenzene was the first compound evaluated during this study and the experimental results are difficult to interpret. The uncatalyzed oxidation of nitrobenzene was evaluated at 200°C with reaction times from 4 to 60 minutes. The loss of nitrobenzene in these runs ranged from 18 to 31% with no apparent relationship between loss of nitrobenzene and reaction time. Inconsistent data were attributed to start-up problems associated with a new operator. The formation of CO_2 in the uncatalyzed oxidations was low, 0.2 to 8.2%, indicating that very little nitrobenzene was being totally oxidized. The addition of catalysts to the experiments at 200°C had little effect on the partial oxidation, or loss, of nitrobenzene. When the reaction temperature was raised to 250°C, the oxidation rate increased to 46% in 60 minutes with 12.2% of the nitrobenzene being completely oxidized to CO_2. Although the results of the nitrobenzene experiments are too varied for detailed analysis, the overall result of the evaluation is that nitrobenzene can be oxidized by the Br-NO_3-Mn system at slow rates.

Pentachlorophenol

The oxidation of pentachlorophenol was evaluated in a series of six experiments. The oxidation rate with no catalysts was measured at reaction temperatures of 165 and 194°C. The results indicate that pentachlorophenol is oxidized by wet oxidation at moderate rates and that the oxidation is complete, as measured by CO_2. However, the addition of the Br-NO_3-Mn catalyst drastically increased the oxidation rate by all three methods of measurement, loss of pentachlorophenol and formation of CO_2 and Cl^-. The initial catalyst reactions with pentachlorophenol were so fast that after 30 minutes at 165°C more than 99% of the pentachlorophenol was partially oxidized. Total oxidation can be achieved with either increased reaction time or increased reaction temperature. The reaction by-products from later experiments were analyzed by GC/MS to identify the partial oxidation products of pentachlorophenol. The only compounds present were dibromochloromethane and bromoform. Such short chained organics are usually the oxidation products prior to the final oxidation to CO_2.

Trichloropropane

The oxidation of trichloropropane was evaluated at a few experimental conditions. The first experiment was an uncatalyzed oxidation at 163°C for 30 minutes. At these conditions, 14.5% of the trichloropropane was oxidized, 5.3% completely to chloride. The next experiments evaluated the effect of adding the catalysts and increasing the reaction temperature. The addition of the Br-NO_3-Mn catalyst doubled the destruction rate by loss of trichloropropane and by formation of CO_2 and Cl^-. These destruction rates were doubled again by increasing the reaction temperature from 165 to 200°C. The ability to oxidize trichloropropane was demonstrated during these 30-minute reactions. The by-products of the reaction were analyzed by GC/MS and identified as debromochloromethane, bromoform, and dichlorobromopropane.

o-Xylene

The oxidation experiments with xylene generated some interesting data. The uncatalyzed oxidation at 165°C destroyed more than half the xylene, 54.3%, but generated only 0.3% of CO_2. The wide difference in destruction rates may be attributable to partial recovery of unreacted xylene with the solvent extraction procedures used, but this was not verified during the xylene oxidation experiments. The destruction rates were increased by the addition of the Br-NO_3-Mn catalysts but not by increasing the reaction temperature.

The most surprising result was the increase in destruction rates caused by increasing the initial concentration of xylene. During these experiments the destruction rate by loss of xylene was greater than 98% with almost half the xylene being totally oxidized to CO_2. This result was also observed with hexachlorobutadiene but the reason for the increase was beyond the scope of this project and was not studied. However, this observation would indicate a slightly higher overall order of reaction for xylene than the first-order rate of reaction observed for the other compounds. Keeping in mind the complexity and number of reactions occurring in the liquid and vapor phases, this slight increase in order may indicate a different reaction mechanism during the destruction process of this compound. The by-products of xylene oxidation were identified by GC/MS as bromoxylene and dibromoxylene. The presence of the brominated by-products reinforces the hypothesis that bromine species are the major oxidant in this catalyst system.

Diphenyl Hydrazine

The oxidation of diphenyl hydrazine is fast and comparable to the oxidation of butyl phthalate. Diphenyl hydrazine was oxidized slowly without catalysts. At 164°C, 19.3% of the initial diphenyl hydrazine was oxidized in 30 minutes and only 3.6% of the initial amount was completely oxidized to CO_2. Addition of the Br-NO_3-Mn catalysts increased the destruction of diphenyl hydrazine to 73.3% in 30 minutes at 164°C, and 44.5% of the initial amount was totally oxidized to CO_2. Increasing the reaction temperature from 164°C to 200°C caused destruction of 97.9% of the initial diphenyl hydrazine in 30 minutes and 69.8% of this initial amount was oxidized completely to CO_2.

Surprisingly, when the initial diphenyl hydrazine concentration was increased from 0.1% to 1.0% the destruction decreased to 57.9% vs. 97.9% by disappearance of organic and 39.5% vs. 69.8% by CO_2 formation. The reason for this sharp decrease was not studied nor was the experiment repeated to confirm this result. The trace by-products of oxidation of diphenyl hydrazine were identified by GC/MS as tribromomethane, various bromobenzenes, and bromodiphenyl hydrazine.

DDT

The oxidation of DDT without catalyst is slow. At 166°C only 9.6% of the initial DDT oxidized in 60 minutes and 2.8% of the initial amount oxidized to CO_2 and 5.6% by Cl^- formation. The addition of the Br-NO_3-Mn catalyst raised the destruction of DDT to 59.8% in 60 minutes at 165°C and 5.4% of the initial material oxidized to CO_2, 19.9% to Cl^- ions. Increasing the temperature to 249°C increased the destruction to 93.5% but did not significantly change the CO_2 or Cl^- destruction numbers. Also, an increase in time from 30 to 60 minutes increased the destruction by only 10.2%. As in the case of butyl phthalate oxidation, the small effect of reaction time on destruction indicates that the oxidation of DDT follows a multistep process.

The destruction of DDT is first-order with respect to initial DDT concentration. Destruction was 100% vs. 98.4% for 0.1% and 1.0% DDT concentration experiments. Experimental conditions were 150°C for 120 minutes for these experiments.

As in the case of butyl phthalate, the actual effects of various catalyst mixtures on the destruction of DDT is minor. The removal of manganese from the catalyst mixture decreases the destruction of DDT and the formation of CO_2 and Cl^- ions. Increasing either bromide or nitrate slightly increases the destruction of DDT as measured by the formation of CO_2 and Cl^- ions.

Analysis of the extractable by-products by GC/MS revealed a variety of materials. By-products formed in an early experiment include bromoform, dibromochloromethane, dichlorobenzene, bromochlorobenzene, dibromochlorobenzene, dichlorophenyl chlorophenyl ketone, chlorophenyl ketone, bromochlorophenyl chlorophenyl ketone, and 1,1-dichloro-2,2-bis(p-chlorophenyl) ethylene. Later experiments include toluene, benzaldehyde, tetrachlorobenzene, dichloroacetophenone, pentachlorobenzene, trichlorobenzaldehyde, and hexachlorobenzene. This variety of by-products from the oxidation of DDT is supportive of the fact that initial experiments supported a multi-path decomposition as indicated by a large disappearance of DDT but a low appearance of CO_2 and Cl^- ions. Although these by-products are somewhat more stable toward oxidation than the original DDT molecule these materials are ultimately oxidized to CO_2, HCl, and H_2O.

Acetonitrile

Acetonitrile is resistant to wet oxidation. Without catalyst only 5.4% of the initial material oxidized in 30 minutes at 165°C. When the catalyst mixture was added, 89.9% of the acetonitrile disappeared at the same reaction conditions. An increase in temperature to 200°C and initial acetonitrile concentration from 0.1% to 1.0% resulted in destruction increasing to 96.3% and 99.3% respectively. An increase in reaction time from 30 minutes to 60 minutes had no effect on the destruction of acetonitrile.

PROCESS DESIGN AND ECONOMICS

With data generated from the batch oxidation reactions of the 15 compounds preliminary capital and operating costs can be estimated for a full-scale continuous process to destroy these compounds. Two processes were designed to destroy aqueous wastes or organic residues.

Process Description: Organic Residues

A continuous large-scale system for the destruction of organic residues by catalyzed wet oxidation is based on the use of a conventional continuous stirred tank reactor (CSTR). The organic residue and compressed air enter the pressure vessel continuously. A reflux condenser returns condensate to the reactor. Noncondensables are scrubbed with caustic and passed through a carbon adsorber. For chlorinated residues it is also necessary to remove HCl from the reactor, which is accomplished through a distillation of the reactor contents and a return of the catalysts to the reactor. Makeup catalysts are also added to the reactor to compensate for losses through the reactor vent.

A CSTR in this system has the advantage of requiring the relatively insoluble and nonvolatile organic to remain in the reactor until it is oxidized to CO_2 or a volatile organic. However these volatile organics are condensed and returned to the reactor through the condensate accumulator. This advantage is more important to a "real world" waste stream composed of easily oxidized or more difficult to oxidize organic compounds. Therefore a CSTR-based wet oxidation system allows for the destruction of the complete range of organics if the design is based on the most difficult to oxidize organic compound.

Process Description: Aqueous Wastes

A large-scale system for the destruction of an aqueous organic waste by catalyzed wet oxidation has the same major components and functions as the organic residue oxidation system. The major difference in these two systems is that any feed water entering the oxidation reactor can only exit the reactor as water vapor. The heat required to boil up this incoming water could be supplied by the heat of combustion of the organic if the organic is at a high enough concentration. The water vapor leaving the reactor is then condensed. The condensate may require subsequent treatment, depending on the particular waste profile being oxidized. All other equipment units function the same as the organic residue process previously described.

Economics

Capital and operating costs were estimated for several catalyzed oxidation processes using the experimental destruction rates obtained in this study. The processes were designed for compounds with different destruction rates to show the impact of destruction rates on the process design and economics. The design basis is a 1000-gal reactor system for destroying a pure compound in water. By fixing the system design at 1000-gal, the major factor affecting the cost of the treatment system is the destruction rate of the organic substance. For example the feed rate of organic for a pentachlorophenol treatment system is 2.3 times the feed rate for a butyl phthalate treatment system. Therefore the corresponding treatment cost per pound of organic would be greater for the butyl phthalate treatment system. However, due to the added constraint of removing hydrochloric acid from the pentachlorophenol system, the operating cost of this system is almost twice the cost of the butyl phthalate system. Therefore, the cost per pound of organic of the pentachlorophenol treatment system is correspondingly higher and approaches the cost of the butyl phthalate treatment system. Other minor factors affecting the treatment costs include air compressor duty, condenser size, cooling water requirements, neutralization or scrubbing requirements, and catalyst losses.

The cost for treating waste organic residues similar to the compounds evaluated in this program ranged from $0.12/lb of organic for compounds with fast destruction rates, such as pentachlorophenol to $1.04/lb for compounds with slow destruction rates such as hexachlorobutadiene. A second type of process was designed to permit the treatment of aqueous waste contaminated with high levels of a soluble organic compound. This process assumes the destruction rate of acetonitrile in a 7.25% aqueous solution and results in costs of $0.45/lb of organic or $0.27/gal of waste.

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SHIPBOARD INCINERATION OF HAZARDOUS CHEMICAL WASTE

Routine Disposal of Liquids
and
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ABSTRACT

In February 1980, an interagency work group undertook a study of at-sea incineration and the alternatives available to the Federal Government for encouraging the design, construction, and operation of U.S. flag incinerator ships. The group examined previous incineration operations, various federal assistance programs, safety and control measures, incinerator ship conceptual designs, environmental impacts, and waterfront facilities. In September 1980, the work group concluded that chemical waste incineration at sea aboard specially designed and equipped vessels is a cost-effective, technically efficient, and environmentally acceptable technology for destroying many combustible hazardous wastes.

The work group was expanded in October 1980, designated the Interagency Review Board for the Chemical Waste Incinerator Ship Program, and now coordinates and expedites all Federal Government activities related to developing an incineration at sea capability in the United States.

This paper presents the findings of the work group and the work program which the Interagency Review Board has initiated. Important ship design factors, such as the regulatory requirements, incinerator technologies, and incinerator system research recommendations, are explained. A conceptual design for a dual-mission ship that can incinerate both liquid and solid wastes is presented. Anticipated operations permits, environmental monitoring, vessel design requirements, and waterfront facilities are discussed.

INTRODUCTION

The United States currently confronts a serious and massive hazardous materials disposal problem. The public health and the nation's environment are being threatened by ever increasing volumes of hazardous wastes. The Environmental Protection Agency (EPA) has estimated that tens of millions of tons of hazardous waste are generated annually across the nation. Furthermore, there are thousands of disposal sites throughout the country being improperly maintained, and a large number may pose health problems. (1-6)

These environmental and public health problems have prompted federal agencies to examine various technologies for treatment and destruction of waste materials. Controlled high temperature incineration, whether on land or at sea, is the most effective method available for the destruction of combustible hazardous wastes. Incineration at sea removes the destruction site from populated areas and the vulnerable freshwater environment, which is of special importance when incinerating the most toxic wastes.

The U. S. faces a deficiency in incineration capacity for chlorinated wastes as well as a difficulty in siting new or expanded incinerators for certain high toxicity or problem wastes. Incineration at sea could provide a significant portion of the needed disposal capacity for short-term as well as a continued long-term disposal option over the next 15 to 30 years.

Several foreign flag incinerator ships have been operating in Western Europe for about a decade. In 1974, 1975 and 1977 three officially sanctioned U.S. at-sea incineration operations were successfully conducted on the foreign incinerator ship, M/T Vulcanus. (The Vulcanus was purchased by a U.S. firm, Chemical Waste Management, Inc., in 1980). Eight shiploads of industrial organochlorine wastes and three shiploads of Air Force Herbicide Orange were destroyed under research, special, and interim permits issued by EPA. These operations and those in Europe have demonstrated incineration at sea of liquid combustible chemical wastes to be an available industrial operation which can be implemented in the U.S. without much of the preliminary testing that other ultimate disposal alternatives may require. (7-16)

In February 1980, an interagency work group (including EPA, Maritime Administration, Coast Guard, and National Bureau of Standards) undertook a study of at-sea incineration technology and the alternatives available to the Federal Government for encouraging the design, construction, and operation of U.S. flag incinerator ships. The work group examined previous incineration operations, various federal assistance programs, safety and control measures, incinerator ship conceptual designs, environmental impacts, and waterfront facilities. In September 1980, the work group issued its report (17) concluding that chemical waste incineration at sea aboard specially designed and equipped ships is a cost-effective, technically efficient, and environmentally acceptable technology for the destruction of many types of combustible hazardous waste.

INCINERATOR SYSTEMS AND RELATED RESEARCH

The Environmental Protection Agency and its predecessor organization have conducted federally supported incineration studies for some 15 years, including 7 years of engineering and scientific studies of hazardous waste incineration technologies, both on land and at sea. These studies have supported increasingly stringent incineration performance and emissions standards of federal, state, and local agencies. Such standards have helped eliminate unsafe incineration practices and have encouraged the development and use of improved technologies to protect public health and the environment.

EPA's work on incineration at sea began in 1974 and continued in 1977, when the Agency permitted and monitored the burning of U.S. industrial and military wastes aboard the incinerator ship M/T Vulcanus. These organochlorine wastes were incinerated at sea with no detectable impact on the environment. The liquid injection incineration equipment on board the ship is similar in basic design to the best available land-based incineration equipment. The major difference between the two technologies is that land-based incinerators for chlorinated materials must have scrubbers to remove effluent acid gases, whereas the marine environment neutralizes the acidic stack emissions from the at-sea incineration process.

Applicable Hazardous Waste

One advantage of incineration is that the energy content of the chemical wastes can be used to maintain combustion, so that wastes assist the destruction process. High energy wastes can even be destroyed without using supplemental fuel. The EPA has studied hazardous waste types and incinerators which can handle different wastes.

Chemical waste streams suitable for thermal destruction fall into four classes:

1. C-H and C-H-O compounds, yielding CO_2 and H_2O
2. C-H-N and C-H-O-N compounds, yielding CO_2, H_2O, and nitrogen oxides
3. C-H-Cl and C-H-O-Cl compounds, yielding CO_2, H_2O, and HCl (gas)
4. Other wastes including organic compounds containing both nitrogen and chlorine; compounds containing sulfur, bromine, fluorine, phosphorus, or silicon; and varied wastes not included in the first three major classes

The candidate wastes for incineration at sea may be either pumpable liquids or slurries, sludges, tars, or discrete solids. The liquids and slurries are highly variable mixtures, with specific gravities as low as .85 or as high as 1.5. The solid wastes also have highly variable physical properties, but they must be suitable for a screw feed or a waste container. A ship that has both liquid injection and rotary kiln incinerators could destroy virtually any organic waste stream, except those containing more than "trace quantities" of heavy metals or other nonincinerable materials which would not be permitted for incineration at sea without appropriate air pollution control devices installed.

Incineration Equipment

Available marine liquid injection incinerators (Figure 1) can safely and effectively dispose of combustible liquid organic chemical wastes. Similar units are used in land-based operations and on the M/T Vulcanus and the K/B Vesta. Although fluidized bed, multiple chamber, and molten salt incinerators are also available today, these designs are not as well developed, proven, or widely used as is liquid injection technology.

The EPA seeks to advance at-sea incineration by investigating the thermal destruction of certain types of solid hazardous wastes including dry flowable granules, containerized wastes, and nonpumpable slurries or semi-solid materials. For destroying these materials, rotary kiln incinerators (Figure 2) have been used for decades in land-based applications. However, at-sea applications would constitute a unique mobile environment for these units, and a research or demonstration period would be necessary. Also, unlike the relatively "ash-free" or "clean-burning" incineration of liquid wastes, many solid wastes contain significant amounts of uncombustible ash materials which must be retained on board and properly disposed of after incineration in the rotary kiln. A stack scrubber might also be needed to prevent particulates from being released with the flue gases.

WASTE TYPES	
PUMPABLE LIQUIDS	YES
SLURRIES SLUDGES	NO
TARS	NO
SOLIDS	
— GRANULAR	NO
— IRREGULAR	NO
— CONTAINERIZED	NO
MAXIMUM OPERATING TEMPERATURE C	1600
MAINTENANCE	LOW
COMMERCIAL APPLICATIONS	WIDELY USED FOR LIQUID WASTES CURRENTLY USED FOR AT-SEA INCINERATION

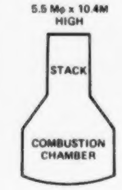

Figure 1. Liquid injection incinerator.

WASTE TYPES	
PUMPABLE LIQUIDS	YES
SLURRIES SLUDGES	YES
TARS	YES
SOLIDS	
— GRANULAR	YES
— IRREGULAR	YES
— CONTAINERIZED	YES
MAXIMUM OPERATING TEMPERATURE C	1600
MAINTENANCE	MEDIUM
COMMERCIAL APPLICATIONS	WIDELY USED ON LAND FOR ALL WASTES

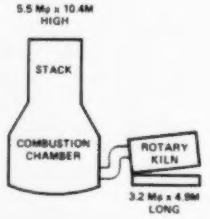

Figure 2. Rotary kiln incinerator.

Recommended Research

A U.S. flag incinerator ship would provide a safe facility to research hazardous waste incineration. To advance shipboard incineration at sea, as well as other vital technology development, the following needs have been identified:

1. Demonstrate full-scale rotary kiln incineration of solid hazardous waste aboard ship;
2. Develop seawater scrubber technology for shipboard incinerators; and
3. Investigate shipboard use of emerging technologies at pilot-scale, such as fluidized bed, molten salt, and oxygen-blown incineration and various air pollution control devices.

These studies would take advantage of available space on an incinerator ship along with supplies of wastes and other facilities. A rotary kiln demonstration program would cost approximately $1.5 million with its associated construction, installation, and engineering evaluation studies. A pilot-scale seawater scrubber program would cost $500 thousand or more. Both programs conducted concurrently would be completed in 12 to 18 months.

INCINERATION AT SEA PERMITS AND ENVIRONMENTAL MONITORING REQUIREMENTS

Permits for Incineration at Sea

The Environmental Protection Agency has permit granting authority for all ocean dumping except dredged material; this authority includes incineration at sea. Ocean Dumping Regulations (18) describe the criteria for permit application and procedures for issuing or denying permits for ocean dumping. EPA regulates incineration at sea according to the Marine Protection, Research and Sanctuaries Act (MPRSA) (19) and the London Dumping Convention (20), applying the Intergovernmental Maritime Consultative Organization (IMCO) mandatory regulations (21) and taking full account of the IMCO technical guidelines (22). A Research Permit is granted for the initial burn of a particular waste and requires extensive monitoring. Special permits, for more routine incineration operations, are granted for a maximum of three years with an option for renewal.

A current revision of the Ocean Dumping Regulations (18) is progressing which will align these rules more closely with the needs of the Chemical Waste Incinerator Ship Program. In addition, further revisions are under discussion which will lead to the development and implementation of policies and procedures for the mixing, blending, and treating of multiple waste streams. It is also acknowledged that the present permit system is time-consuming, costly, and inflexible. A solution to this regulatory problem in support of incineration at sea is of prime concern to EPA.

Under the present system, a permit application must describe specified chemical and physical characteristics of the waste and the results of specified tests done on the waste. The method of incineration, the proposed incineration location, and any special considerations regarding probable impacts of the disposal must also be included. A permit application is reviewed in consultation with other federal, state, and local agencies. After a tentative determination is reached, time is allowed for public comments, which may include a public hearing. When all information has been collected and evaluated, a final determination is made and announced. Administrative appeal procedures and resource to legal authority are available if anyone objects to the action of the permitting authority.

The design and operation requirements for land-based and shipboard incineration systems are divided into three main categories: regulatory, technical, and safety. (23) The regulatory requirements include the ocean dumping permit requirements, the Resource Conservation and Recovery Act (24) requirements which regulate the land-based portion of the integrated system, and the pertinent Coast Guard and IMCO requirements. IMCO mandatory regulations and technical guidelines are considered as technical requirements, and all may appear in the permit.

Open ocean sites for at-sea incineration are selected to minimize the interference of waste disposal activities on the marine environment. Disposal site evaluations are based on EPA criteria. The results of these studies are presented as an environmental assessment of the impact of using the site for disposal. An environmental impact statement is subsequently prepared for each site designation. (8,25)

A site has been designated in the Gulf of Mexico and one has been proposed and evaluated for the North Atlantic.

Environmental Monitoring

Environmental monitoring during at-sea incineration is imposed by the MPRSA regulations and the IMCO mandatory regulations adopted under the London Dumping Convention. The IMCO mandatory regulations, which went into effect in the United States in March 1979, impose minimum operational monitoring requirements for protection of the marine environment. Additional requirements may be in the permit for at-sea incineration. For example, specific permit monitoring requirements were imposed on the at-sea disposal actions for organochlorine waste and Herbicide Orange. Two general cases involving different degrees of environmental monitoring are discussed below.

Initial Incineration Monitoring--

The London Dumping Convention and the MPRSA require a survey during the first use of an at-sea incineration facility to determine compliance with the regulations. The survey requires stack gas sampling and analysis; monitoring of the stack gas for CO, CO_2, O_2, total hydrocarbons, and haloenated organics; and combustion and destruction efficiencies of at least 99.9 percent. The survey must be repeated every two years.

Monitoring in excess of the minimum regulatory requirements would be performed, for example, under the following conditions:

1. An unusually hazardous waste (e.g., PCBs, which may contain TCDFs) or a waste containing an unusually hazardous substance (e.g., Herbicide Orange and its 2,3,7,8-TCDD contaminant) is to be incinerated.
2. A new type of waste is to be incinerated, unless it is deemed similar to a previously tested waste.
3. A new incinerator or a new type of incinerator is used, or extensive system component changes are made.

When any of these three situations occur, it is expected that detailed stack sampling followed by shipboard or land-based analysis of the samples will be required. Additionally, monitoring of solid residue from a rotary kiln incinerator and influent and effluent from a scrubber would be required.

When waste containing appreciable amounts of sulfur and/or nitrogen (e.g., greater than 5 percent) are incinerated, stack gases should be monitored for oxides of sulfur and/or nitrogen. Additionally, during any research phase, oxides of nitrogen should be monitored to establish baseline values. In some cases, seawater sampling could be required to determine actual impacts of incinerator effluents on the sea and on marine organisms. For example, marine water and organism sampling was performed during several Research Permit burns of organochlorine waste in the Gulf of Mexico, and marine waste samples were taken during the Research Permit burn of Herbicide Orange in the Pacific Ocean.

Routine Incineration Monitoring--

The MPRSA regulations and London Dumping Convention mandatory regulations do not require environmental monitoring during routine operations. These regulations do, however, require operational monitoring. The operational monitoring requirements are:

1. Flame temperature not less than 1250°C, unless studies on the incinerator have shown that a lower temperature will achieve the required combustion and destruction efficiencies.
2. Combustion efficiency is at least $99.95 \pm 0.05\%$, based on

   $$\text{Combustion Efficiency} = 100 \times \frac{C_{CO_2} - C_{CO}}{C_{CO_2}}$$

   Where C_{CO_2} and C_{CO} are, respectively, concentrations of carbon dioxide and carbon monoxide in the stack gas.
3. No black smoke or flame extension above the exit plane of the stack.

The London Dumping Convention mandatory regulations also direct that Contracting Parties "take full account of the technical guidelines." The IMCO technical guidelines establish additional operational standards. Several relevant guidelines are:

1. Minimum 3 percent oxygen in stack gas near the exit plane of the stack.
2. Incinerator wall temperature should be not less than 1200°C (unless tests on the unit have shown that adequate waste destruction can be achieved at lower wall temperatures).
3. Residence time of all wastes in the incinerator should be of the order of one second or longer at a flame temperature of 1250°C.
4. Waste type and rate of input to the incinerator should be recorded.

WATERFRONT SUPPORT FACILITIES

Waterfront integrated hazardous waste management facilities are necessary to support incinerator ships. Such a facility would include waterfront storage tanks; waste receiving, processing, and handling equipment; a laboratory for waste analysis, and a transfer terminal for loading wastes aboard ship. In addition, an inland transportation system is required to safely haul wastes to the waterfront facility. (16,17)

The waterfront facility must:

1. Receive liquid and solid hazardous wastes either by land or by waterborne barge transport;
2. Analyze, blend, shred, and process the materials as appropriate for incineration at sea;
3. Load the waste aboard ship in a safe and efficient manner; and
4. Remove and receive residues from the incinerator ship for analysis and disposal either on land or at sea, in the case of incineration of wastes producing a collectable residue during disposal.

The facility will accommodate waste in almost any physical form and in several types of containers, some of which may be older, corroded, and possibly leaking. Ideally, the facility would service three transportation modes for delivery of wastes: truck, rail, and barge. It should consecutively accommodate at least two incinerator ships, each on a 10 to 14 day cycle. Figure 3 presents a conceptual layout of the facility.

Liquid waste, solid waste, and ash residue from incineration will be processed and stored separately. Liquid waste in drums and other containers will be sent through a shredder in the dedrumming facility. Liquid from both the containers and the decontamination of the containers will be blended to optimize transfer and combustion processes and pumped to storage tanks. Liquid waste arriving in tank trucks or tank cars, along with the tanker decontamination rinse, will also be blended and pumped to the storage tanks.

Solid waste arriving at the site will be unloaded at the unloading rack, prepared for incineration by shredding, and placed in bulk material containers to be loaded on the ship. Any ash residue from the at-sea burn will be returned to the waterfront facility and kept in the residue storage area until removed for ultimate disposal, probably in a landfill approved for hazardous waste disposal.

DUAL-MISSION INCINERATOR SHIP

Design Alternatives and Operating Scenario

In addition to a conventional ship, several alternative marine technologies may be viable for an incineration at sea system capable of destroying solid as well as liquid waste, including:

1. Integrated tug/barge unit (a ship-shaped barge propelled by a specially designed pushing tug that is mechanically linked to the barge stern).
2. A towed tug/barge combination (a traditional tug and tethered incinerator barge).
3. A ship conversion (an existing tanker may be the most easily converted ship).
4. A tug/supply vessel (using either existing vessels or new vessels).

A conventional new ship design was selected, based on the following operating scenario:

1. Two week operating cycle, with ten days "on-site;"
2. Both liquid and solid wastes accepted;
3. Three liquid incinerators operated continuously at full capacity for ten

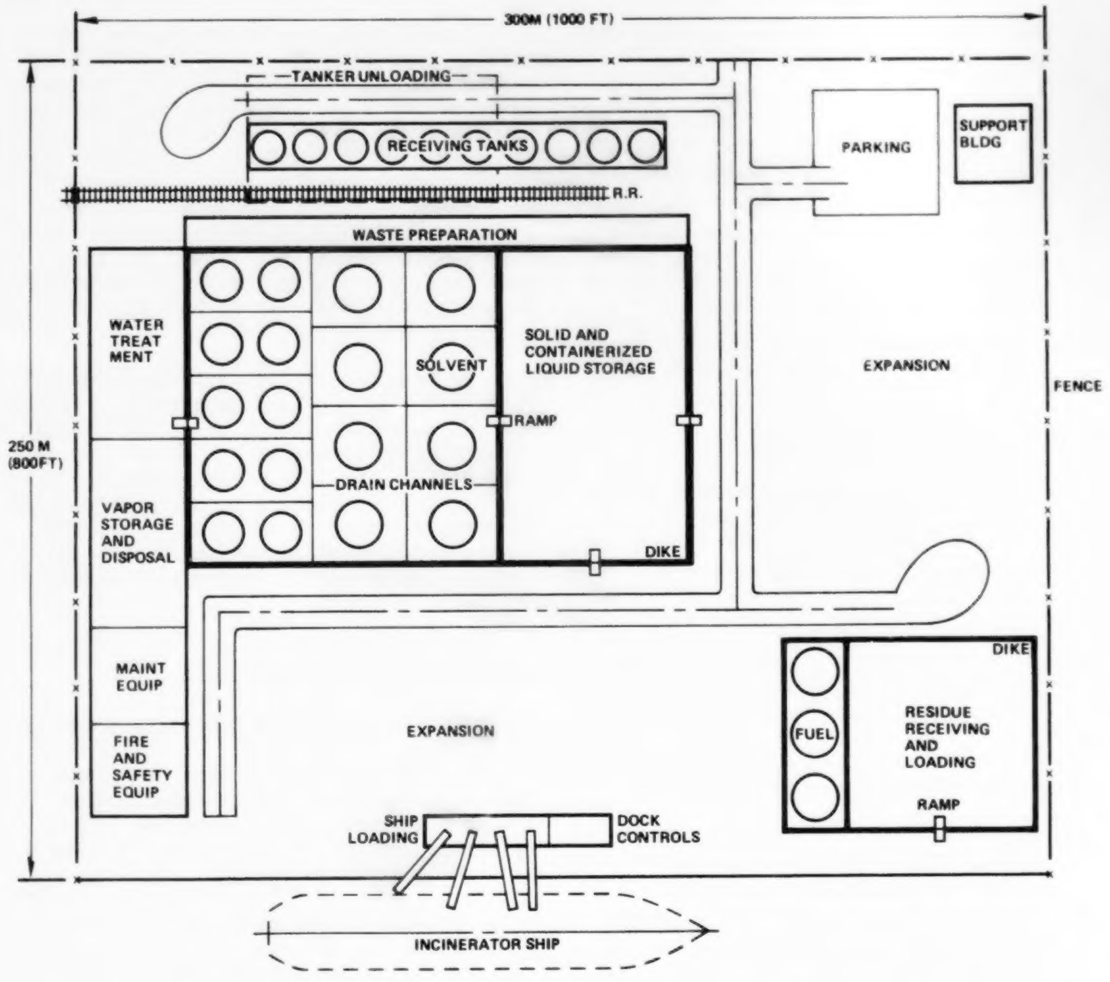

Figure 3. Waterfront facility layout.

days for routine destruction of large volumes of liquid wastes;

4. One solid waste incinerator operated for research purposes;
5. No "abandoned site" wastes accepted without prior analyses;
6. Solid waste containerized before loading onto ship;
7. Wastes loaded at terminal by automatic equipment;
8. Drifting or slow steaming during incineration operations; and
9. Heading into wind maintained by bow thruster during incineration.

Adopting a dual-mission scenario has resulted in a conservative conceptual design that exceeds the needs of a vessel built only for routine liquid incineration. A first-generation U.S. flag commercial incinerator vessel need not incorporate all the features of this design.

Incinerator Ship Conceptual Design

A typical mild steel tankship hull, as shown in Figure 4, has been equipped with extensive auxiliary processing systems to handle and incinerate liquid and solid hazardous chemical waste. The incineration plant, liquid cargo pumps, and

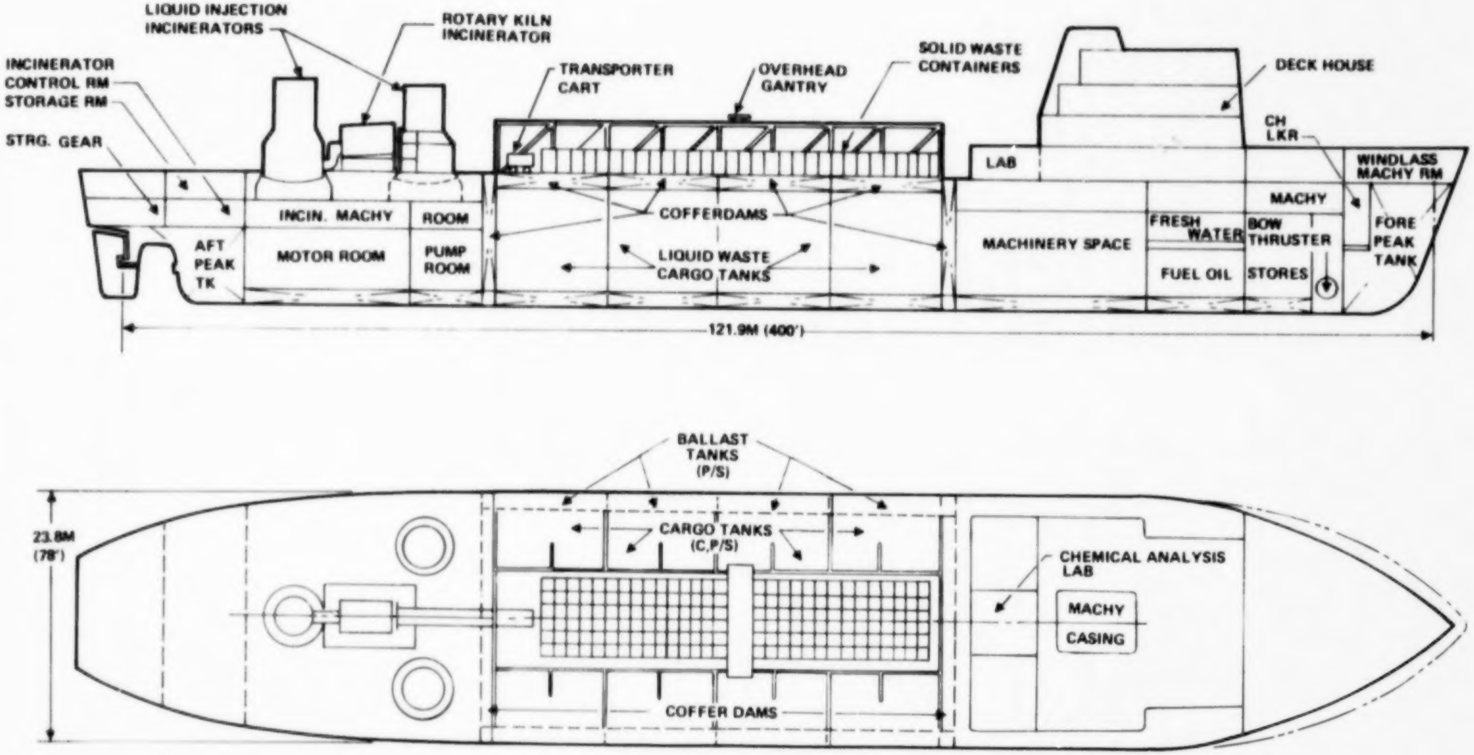

Figure 4. Incinerator ship conceptual design: IMCO Type I/Type II Combination Hull

unattended electric propulsion motors are located aft, with the deckhouse, laboratory, and attended propulsion diesel-generator machinery spaces located forward. This arrangement locates personnel living and working spaces as far as possible from the incinerator plume, heat, and potential chemical contamination. Design specifications of the dual-mission incinerator ship are presented in Table 1.

Liquid waste tanks and solid waste container storage are midships. The four centerline tanks provide IMCO Type I cargo protection. The eight port and starboard tanks, which are protected by wing ballast tanks, are ample for Type II cargo protection. Type I chemicals are products that require maximum preventive measures to preclude escape of such cargo; Type I products require significant preventive measures to preclude escape. (26,27) The large amount of ballast tankage can be sequentially filled to help the ship maintain a constant draft and uniform ship motions as wastes are incinerated. Solid waste containers are stored on deck, directly above the liquid waste tanks, but separated from those tanks by a three foot high inert gas-filled void across the full width of the cargo area.

The rotary/kiln liquid injection incinerator combination is on the ship centerline, with the two liquid injection incinerators located out-board of the kiln's forward end. The rotary kiln is an experimental facility and the problems of safely loading, handling, and incinerating the solid wastes have influenced the overall design in several respects. The kiln axis on the ship centerline minimizes the effect of ship's roll on the waste residence time. The estimated maximum ship pitch angle of about 2 1/2 degrees is unlikely to disrupt the rotary kiln's operation. The ship's vibrations and roll motions impose loads on the kiln's external rotary drive, but two major induced vibration sources, the propulsion motors and the propeller, would be idle much of the time that the rotary kiln is operating. The diesel generators, another major source of induced vibration, are forward, remote from the incinerators. Therefore, ship source vibrations should not disrupt the rotary kiln. Isolation mountings and a modified rotary drive can be provided to alleviate the effect of vibration and roll.

The ship is powered by a diesel electric propulsion plant, providing a service speed of 12 Kts. The propulsion motors must be located aft, but the diesel generators are below the forward deckhouse, so that the machinery space, where the engineers will work most of the voyage, is separated from both the incineration system and the waste cargo. The same diesel generators power the incineration plant when the propulsion plant is idle or operating at reduced speeds. This "power pool" arrangement makes possible a single installation, rather than separate ship's propulsion and ship's service generator installations.

TABLE 1. INCINERATOR SHIP DESIGN SPECIFICATIONS

Length Overall		129.5m (425'-0")
Beam, Molded		23.8m (78'-0")
Draft, Full Load		7.5m (24'-7")
Range		5000 Nautical miles
Liquid Waste Capacity		7200 mt (7088 long tons)
Solid Waste Capacity		360 mt (355 long tons)
Incinerator Specifications		
	Liquid	Solid
Number	3	1
Flame Temperature	Up to 1600°C	Up to 1600°C
Capacity	10 mt/hr (each)	1.5 mt/hr
Residence Time	1 to 1.5 sec	Minutes to hours

TABLE 2. ESTIMATED SHIP CONSTRUCTION AND OPERATING COSTS

Contract Drawings	\$ 1 million
Construction Contract (1)	\$50 million
Plan Approval, Inspection, and Spares	\$ 1 million
Total	\$52 million
Projected Ship Cost (2)	\$75 million
Operating Cost (3)	\$ 1.1 million/14 day voyage
Ship Related Disposal Cost	\$145/metric ton of waste

(1) Includes \$14 million for subcontracted incineration systems.

(2) Based on October 1982 contract award and March 1985 vessel delivery, assuming 10% annual inflation rate.

(3) Based on 1985 start of operations.

Estimated Costs and Schedule

Ship construction cost is conservatively estimated at \$75 million for vessel delivery in 1985 (Table 2). Thirty months total construction time is required. Operating cost includes ship capital cost depreciated over 15 years, but does not include waterfront terminal operations or waste land transportation costs.

CONCLUSION

Incineration at sea aboard specially designed and equipped ships has been determined to be a cost-effective, technically efficient, and environmentally acceptable technology for the destruction of many types of combustible hazardous waste, including chlorinated organic chemical and petrochemical wastes (17). An Interagency Review Board for the Chemical Waste Incinerator Ship Program has been formed to coordinate and expedite all Federal Government activities related to incineration at sea. (28) Principal participants at this time are the Environmental Protection Agency, Maritime Administration, Coast Guard, and National Bureau of Standards. The work program of the Interagency Review Board includes the following projects:

1. Investigation and pursuit of viable legislative amendments to provide additional federal assistance for U.S.-flag incinerator ship development;
2. Establishment of a coordinated certification and permitting program for an applicant who wishes to establish a commercial incineration at sea service;
3. Encouraging and assisting state and local authorities to develop waterfront integrated hazardous waste management facilities to support incinerator ships;
4. Development of technical requirements based on existing international standards and national regulations for the design and operation of incinerator ship systems;
5. Planning and conducting research to advance the state-of-the-art of incineration at sea, e.g., polymeric liner materials for containment of hazardous wastes, kinetics of the incineration process, and incineration of solid wastes at sea;
6. Evaluation of loan guarantee applications from private industry for U.S.-flag incinerator ship development; and
7. Environmental assessment and designation of ocean incineration sites.

Early in 1981, the National Advisory Committee on Oceans and Atmosphere (NACOA) released a Report to the President and Congress entitled, "The Role of the Ocean in a Waste Management Strategy." (29) This special report is the culmination of a two-year effort by NACOA to formulate recommendations on use of the ocean as a waste disposal medium. NACOA is firmly convinced that the United States must reexamine present national policies and regulations concerning waste disposal in the oceans, and notes a high probability that land, deepwell, and atmospheric waste disposal activities will be reduced during the 1980's in favor of ocean waste disposal. NACOA recommends that ocean disposal of industrial wastes should continue at sites where evidence indicates no unreasonable environmental degradation and when human health, environmental, and economic considerations indicate this is the preferable option. It is the opinion of this paper's authors that chemical waste incineration at sea, when properly regulated and controlled, thoroughly satisfies these NACOA criteria and will be a preferred, readily available, disposal option for many hazardous wastes.

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The authors wish to express their sincere gratitide to the members of the Interagency Review Board for the Chemical Waste Incinerator Ship Program and its predecessor, the Interagency Ad Hoc Work Group, for their contributions to this program.

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29. National Advisory Committee on Oceans and Atmosphere, A Special Report to the President and Congress - The Role of the Ocean in a Waste Management Strategy, January 1981.

ELIMINATION OF HAZARDOUS WASTES BY THE MOLTEN SALT DESTRUCTION PROCESS

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ABSTRACT

The Resource Conservation and Recovery Act (RCRA) imposes strict regulations on the management of hazardous wastes. Disposal of the wastes by any means that does not result in conversion of the waste matter to ecologically harmless materials sets up a continuing responsibility for prevention of damage to public health and to property. Under RCRA, the waste generator must bear this continuing responsibility with its concomitant liability potential. The generator's responsibility, however, can be terminated by destruction of the waste material in conformance with RCRA regulations, which require at least 99.99% destruction and removal efficiency (DRE) of all principal organic hazardous constituents (POHC). An exception to this rule is polychlorinated biphenyls (PCBs) for which a minimum of 99.9999% DRE is required. To meet these stringent requirements, much attention is being given to high-temperature combustion systems for hazardous waste treatment. This paper describes the Rockwell Molten Salt Destruction (MSD) process and recent experimental results which demonstrate the high degree of destruction achievable with the MSD process. These experiments were conducted with the support of the EPA, Incineration Research Branch, Contract 68-03-3014, TMS II, Task 21, Subtask 1. These tests emphasized the treatment of chlorinated hydrocarbons with MSD. Results of prior MSD tests performed with a variety of hazardous waste materials are also described herein.

MOLTEN SALT DESTRUCTION PROCESS

This process is based on the use of a molten salt, such as sodium carbonate, as a heat transfer and reaction medium. In the process, combustible waste and air are continuously introduced beneath the surface of a sodium carbonate-based salt at 1450 to 1850°F. Figure 1 shows the molten salt combustor schematically. The combustible material is added in such a manner that any gas formed during combustion is forced to pass through the melt before it is emitted into the atmosphere. The off-gas containing carbon dioxide, steam, nitrogen, and unreacted oxygen is cleaned of particulates in commercial applications by passing it through a baghouse.

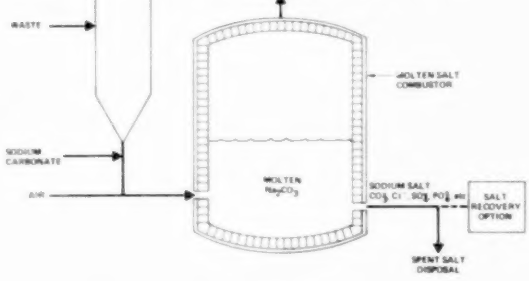

Figure 1. Schematic of molten salt waste combustion system.

Acidic gases, such as HCl and SO_2, produced from halogenated organic compounds and sulfur-containing organic compounds, respectively, are neutralized and absorbed by the alkaline Na_2CO_3. The ash introduced with the combustible waste is also retained in the melt. The char from the fixed carbon is consumed in the salt. The temperatures of oxidation are too low to permit a significant amount of NO_x to be formed by fixation of the nitrogen in the air.

The scrubbing function of the sodium carbonate leads to the formation of other sodium salts. Ash, introduced by the waste, must be removed when it becomes excessive to preserve the fluidity of the melt. An ash concentration of about 20 wt % provides an ample margin of safety for the melt fluidity. In some applications, the melt can be removed batchwise. In other applications, a side stream of the melt is withdrawn either batchwise or continuously and is processed. If desired, the melt may be quenched in water, the solution filtered to remove the ash, and processed to recover the carbonate which is then recycled to the combustor.

Sodium carbonate is used because it is compatible with combustion products, CO_2 and H_2O, and because it reacts with acidic gases such as HCl (produced from organic chloride compounds). It is stable, nonvolatile, inexpensive, and nontoxic.

Data are reported from tests conducted in two different-sized systems. One system is a 6-in.-diameter bench-scale unit for feasibility and optimization tests (up to approximately 3 lb/h). The other system is a pilot-scale unit (up to approximately 250 lb/h) for obtaining engineering data for the design of an actual plant.

DESTRUCTION OF HEXACHLOROBENZENE AND CHLORINE

A program to test the destruction of solid hexachlorobenzene (HCB) and liquid chlordane by the MSD process was completed for the Environmental Protection Agency under Contract 68-03-3014, Task 21, Subtask 1. The HCB was selected as a stand-in for PCBs; chlordane was selected as an example of a liquid organic chlorinated waste. The experimental portion of the program consisted of bench-scale tests and pilot-scale tests.

Bench-Scale Tests

Test Apparatus and Waste Streams

The overall objective of the bench-scale tests was to provide a data base for the pilot-plant tests. A schematic of the bench-scale combustor is provided in Figure 2.

The hexachlorobenzene, mixed with coke (70 wt % HCB — 30% coke) to increase the heating value, contained (on a weight basis) 98% HCB and 2% inerts. The chlordane, mixed with kerosene (60 wt % chlordane, as received — 40% kerosene), contained 61.1% carbon, 27.8% chlorine, and 8.7% hydrogen.

HCB-coke feed rates varied from 1.7 to 3.2 lb/h, and chlordane-kerosene feed rates varied from 0.9 to 1.4 lb/h. The

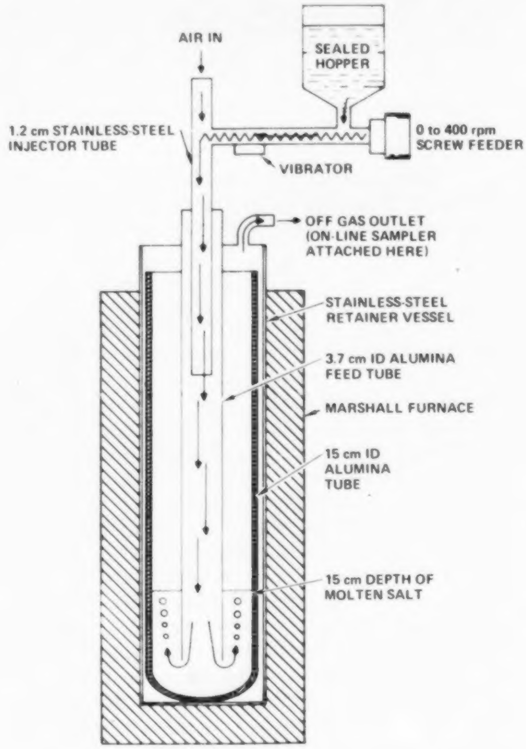
AIR IN
SEALED HOPPER
1.2 cm STAINLESS-STEEL INJECTOR TUBE
0 to 400 rpm SCREW FEEDER
VIBRATOR
OFF GAS OUTLET (ON-LINE SAMPLER ATTACHED HERE)
STAINLESS-STEEL RETAINER VESSEL
3.7 cm ID ALUMINA FEED TUBE
MARSHALL FURNACE
15 cm ID ALUMINA TUBE
15 cm DEPTH OF MOLTEN SALT

Figure 2. Bench-scale molten salt combustor schematic.

air feed rate was 2.5 scfm. The superficial air velocity through the melt was 1 ft/s. The NaCl content of the melt increased with the amount of waste processed. It reached 88 wt % in the case of HCB and 55 wt % in the case of chlordane.

Sampling and Analysis Procedures

Portions of the off-gas were sampled with a sampling line consisting of: (1) a heated glass fiber filter which removed particulates, (2) a heat exchanger which cooled the gas to a proper absorption temperature, and (3) polyurethane foam plug(s) which capture the HCB or chlordane in the off-gas followed by toluene-containing impingers to trap any material which escaped the polyurethane foam plug. These samples, along with samples of the melt, were analyzed for undestroyed HCB and chlordane. The sampling and chemical analyses for HCB and chlordane were done in accordance with EPA-approved modifications to EPA Methods 612 and 608, respectively. A gas chromatograph equipped with an electron capture detector was used in this analysis. A schematic of the sampling train for capturing undestroyed HCB and chlordane is shown in Figure 3.

The analytical procedures described below follow the methods recommended in EPA Methods 608 and 612 for organochloride pesticides.

Sample Extraction and Connection. The polyurethane plug and glass fiber filter were placed in Soxhlet extractors and extracted with methylene chloride for about 10 h. Melt samples were dissolved in water. The resulting solutions were then extracted with methylene chloride using a separatory funnel. The extracts were quantitatively transferred to Kuderna-Danish (K-D) evaporators. When the apparent volumes of each extract reached 1 to 2 ml, the K-D apparatus was moved and allowed to drain while cooling. Fifty (50) ml of hexane was added to each extract, and the resulting solutions were then concentrated to a final known volume of 1 to 5 ml. Known aliquots of impinger solutions and probe washings were directly injected into the gas chromatograph for analysis.

Gas Chromotographic Analyses. Analyses of hexachlorobenzene and chlordane were conducted using a chromatograph with an electron capture detector. The chromatographic column was a 6-ft x 4-mm-ID glass column packed with 100/120 Supelcoport coated with 1.5% SP2250 and 1.95% SP2401. This column is recommended in EPA Method 608 for organochlorine pesticides and PCB analyses. Confirmation of hexachlorobenzene or chlordane was done on selected samples by a gas chromatograph-mass spectrometer (GC-MS) using characteristic ions at m/e 284 for HCB and m/e 373 for chlordane. Only the electron impact mode was used in this GC-MS work. Degradation products were also analyzed, and their mass spectra was searched and compared to EPA/NIH or special priority pollutant libraries to identify the most probable chemical compounds. The GC-MS analysis of the samples has shown mainly the presence of unburned hydrocarbons anthracene and other polynuclears along with some chlorinated derivatives (during off-spec conditions). Furans and dioxins were not detected using conventional GC-MS analysis.

HCB Results

The results of the HCB destruction tests are shown in Table 1 and include the concentration of HCB in the off-gas and in the melt as well as the destruction removal efficiency. The destruction removal efficiency is defined as 100% minus the percent of HCB in the feed emitted to the atmosphere and thus does not include the contribution from the melt. No HCB was detected in any of the melt samples, despite the very low detection limits (less than 1 ppb) for HCB.

Excellent destruction was obtained in all cases. The best destruction removal efficiency, greater than 7/9's (>99.9999986%), was obtained at 1839°F with 118% of stoichiometric air. Excellent destruction removal efficiencies were also obtained at 127% stoichiometric air and 1656°F (>99.999974%) and at 70% stoichiometric air and 1848°F (>99.999982%) The last result indicates excellent destruction even when excess air is not used.

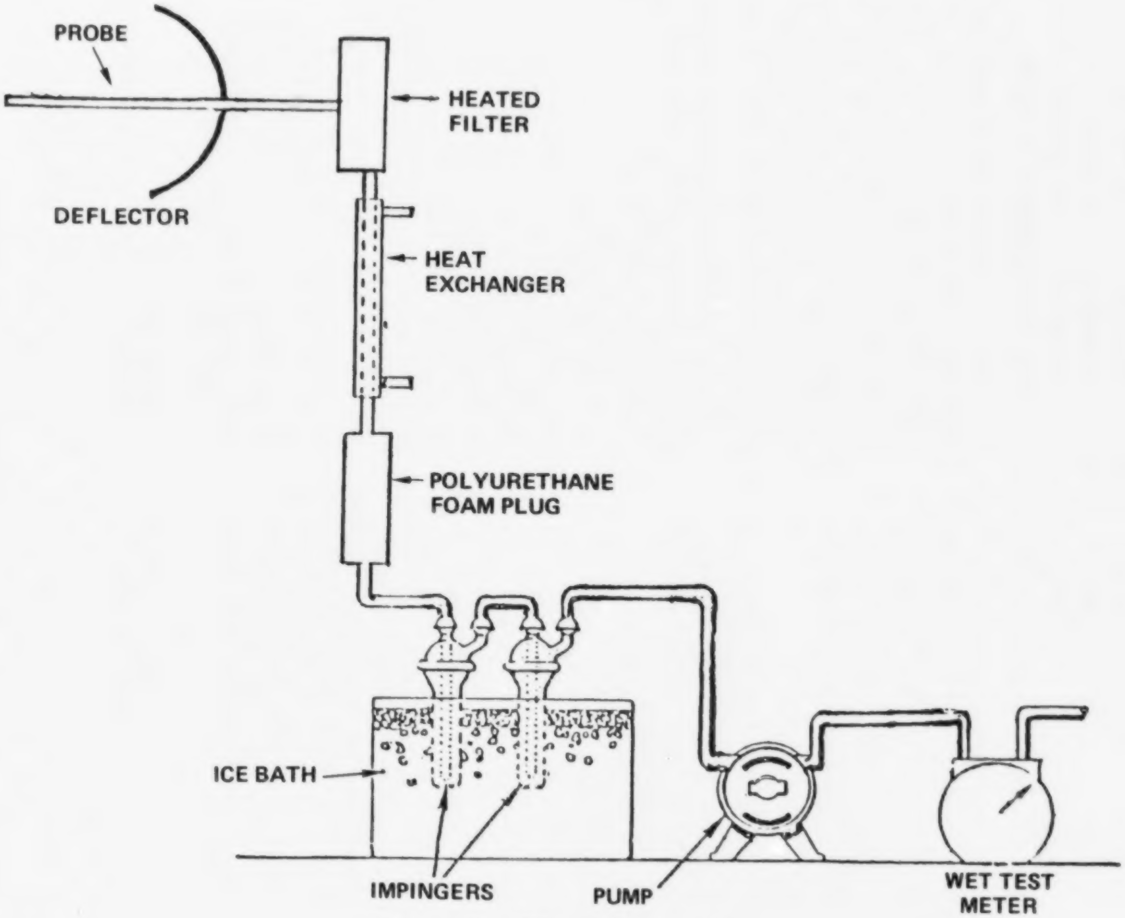

Figure 3. HCB sampling system.

TABLE 1. SUMMARY OF HCB RESULTS

Temp (°F)	% stoich air	Conc of HCB in off-gas		Conc of HCB in melt (ppmw)	Destruction removal efficiency (%)
		ppmv	mg/m^3		
1839	118	<0.00017	<0.0019	<0.00100	>99.9999986
1848	70	<0.0031	<0.037	<0.00040	>99.999982
1656	127	<0.0028	<0.033	<0.00110	>99.999974

No HCB was detected in any melt sample even though melt samples were taken while HCB was being fed. Thus, the concentration of HCB in the melt was, at most, 1 ppb in spite of the short residence time of the feed in the expanded melt (∿3/4 s). This is an excellent indication that the spent melt is nontoxic.

The concentration of HCB in the off-gas was extremely low in all cases. In the 1839°F test with excess air, the concentration of HCB was only 0.00017 ppmv or 0.0019 mg/m^3. In the 1656°F test and in the test with 70% of stoichiometric air, the concentrations were higher by an order of magnitude but still extremely low (0.003 ppmv or 0.03 mg/m^3).

Chlordane Results

The results of the chlordane destruction tests are shown in Table 2.

The sensitivity of the electron capture detector is significantly less for chlordane (60 ng/ml) than for HCB (1 ng/ml) due to the relative chlorine contents of the molecules and the number of different chlordane compounds in the feed. Thus, the detection limits were considerably higher than those of HCB.

Excellent chlordane destruction was obtained in the excess air tests. In these tests, two peaks with the same elution times as two of the four characteristic chlordane peaks were present. These peaks were assumed to be chlordane for the calculation of destruction removal efficiencies. With this conservative assumption, the destruction removal efficiencies were greater than 99.9999%.

In the test with 81% of stoichiometric air, in which larger peaks were found, three peaks with the same elution time as three of the four characteristic chlordane peaks were present in all samples except the impinger and the melt sample. However, when the first plug was examined by gas chromatograph-mass spectrometry, the three peaks with elution times similar to chlordane were identified as not due to chlordane isomers. Thus, the chlordane destruction efficiencies were probably much greater than 99.99%, which was calculated assuming the three "chlordane" peaks were actually due to chlordane.

No chlordane was detected in any melt sample even though melt samples were taken while the chlordane was being fed. Thus, the concentration of chlordane in the melt was, at most, 12 ppb.

TABLE 2. SUMMARY OF CHLORDANE RESULTS

Temp (°F)	% stoich air	Conc of chlordane in off-gas		Conc of chlordane in melt (ppmw)	Destruction removal efficiency (%)
		ppmv	mg/m^3		
1930	121	<0.00132	<0.0447	<0.0090	>99.9999951
1836	81	<0.243	<4.08	<0.0120	>99.9934
1648	118	<0.00267	<0.0220	<0.0080	>99.999903

The concentration of chlordane in the off-gas was very low. In the 1830°F test and in the 1648°F tests (both with excess air), the concentration of chlordane was <0.001 and <0.003 ppm, respectively. The concentration of chlordane in the test with 81% of stoichiometric air was <0.243 ppm. However, the fact that the peaks (at least in the plug) could not be confirmed as chlordane by the GC-MS indicates that the chlordane concentration is much less than this value.

Pollutant Concentrations from HCB and Chlordane Tests

No chlorine or phosgene was detected in the off-gas. The limits of detection of chlorine and phosgene are 0.2 and 0.3 ppmv, respectively. The HCl concentrations were <100 ppm. No H_2 or CH_4 was detected except with less than 100% of stoichiometric air. As expected, the NO_x levels were very low (<50 ppm). The CO levels were higher than desired (up to 2.4%) in the excess air tests. Such high values have been noted before in this laboratory when chlorinated aromatic compounds were destroyed in Na_2CO_3 melts containing large amounts of NaCl. However, the CO concentrations decreased markedly with increasing melt temperature and with increasing percent stoichiometric air. While destruction efficiency and destruction removal efficiencies of 99.9999% and better can be achieved with excess air at 1830°F and at 1648°F, a temperature of 1830°F is preferred over 1648°F since CO emissions are much lower at the higher temperature.

Pilot-Scale Tests

The Molten Salt Test Facility (MSTF) was operated for a total of 96 h to provide five data points each for demonstrating destruction of HCB and chlordane. A schematic of the MSTF, including the two sample locations used for these experiments, is shown in Figure 3. Sample Location 1 was immediately after the molten salt destructor, i.e., just upstream of the particulate drop box. Sample Location 2 was just downstream of the baghouse. The feed rates of HCB and chlordane were as high as 269 and 72 lb/h, respectively, in these tests. The tests were conducted at melt temperatures from 1645 to 1816°F and from 78 to 151% of stoichiometric air. Sampling for unreacted HCB and chlordane was done in the exhaust of the molten salt combustor, in the exhaust of the particulate baghouse downstream of the combustor, in the residual baghouse salt bottoms, and in the salt melt overflow from the combustor.

The maximum total air feed rate corresponded to a 2.7-ft/s superficial velocity in the bed. Testing was done in 0.5- to 2.0-h test periods with a minimum 1 h of vessel purging and up to 3 h of process stabilization between sampling periods. Destruction gas sampling was done during each sampling period. Auxiliary coke fuel was used throughout the various waste burn periods as required to maintain nominal operating conditions. Between burn periods, coke or diesel oil was the only combustible material fed to the vessel. The salt bed composition in all cases was maintained at 50 wt % sodium chloride and 50 wt % sodium carbonate to simulate nominal steady-state bed compositions for organochloride waste destruction.

HCB Test Results

The HCB feed rate varied from 46 to 269 lb/h. Coke was used as auxiliary fuel in all tests except 3B, where no auxiliary fuel was needed. Bed temperatures varied from 1685 to 1805°F.

The test results are summarized in Table 3. Runs 1 and 2A were conducted essentially under the same test conditions. An HCB concentration of 0.27 $\mu g/m^3$ was determined in the combustor exhaust (Sample Location 1) on Run 1 using a plug sampler. On Run 2A, no HCB was detected in the combustor exhaust using an impinger sampler (HCB 0.8 $\mu g/m^3$). No HCB was detected in the exhaust from the baghouse (Sample Location 2) for Run 1. Based on the HCB detection limit and the size of the baghouse gas sample, this resulted in an HCB concentration in the final system exhaust of less than 0.006 $\mu g/m^3$. An HCB sample was not taken in the baghouse

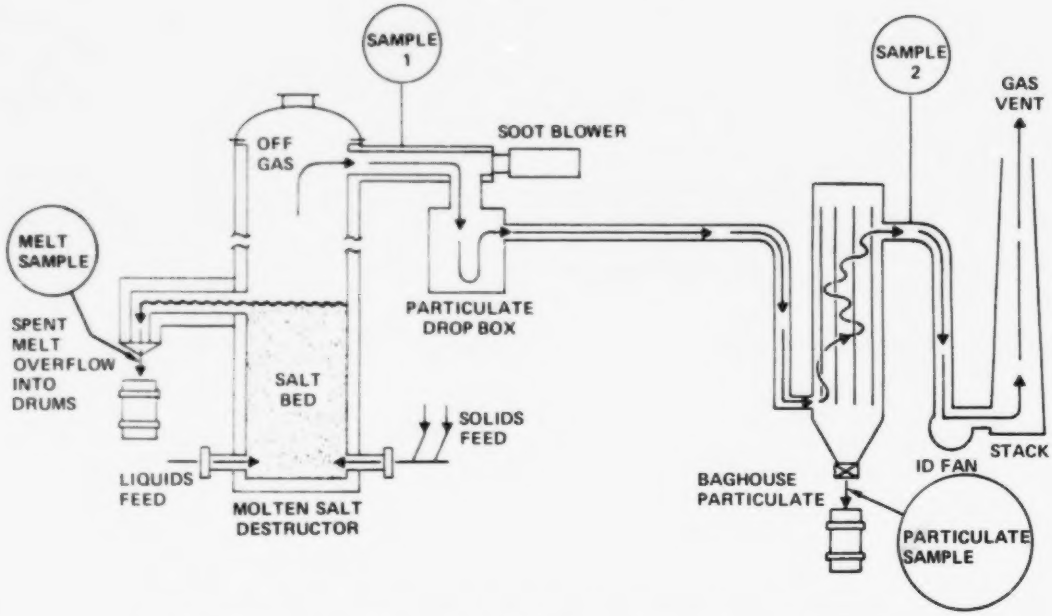

Figure 4. Molten Salt Test Facility including sample locations.

TABLE 3. SUMMARY OF PILOT-SCALE TEST RESULTS

	HCB	Chlordane
Combustor off-gas		
mg/m^3	$2.7 \times 10^{-4} - 7.1 \times 10^{-2}$	$5.3 \times 10^{-3} - 6.8 \times 10^{-2}$
ppmv	$2.3 \times 10^{-5} - 6.1 \times 10^{-3}$	$3.2 \times 10^{-4} - 4.1 \times 10^{-3}$
Baghouse		
mg/m^3	$<6 \times 10^{-6} - 1.6 \times 10^{-4}$	$<3.6 \times 10^{-4} - <4.4 \times 10^{-3}$
ppmv	$<5.2 \times 10^{-7} - 1.4 \times 10^{-5}$	$<2.1 \times 10^{-5} - <2.6 \times 10^{-4}$
Spent melt, ppmw	0.001 – 0.104	0.0044 – 1.2
NO_x, ppmv	70 – 125	0.5 – 630
HC, ppmv	35 – 110	0.4 – 60
Particulate, mg/m^3	$<6.2 \times 10^{-3} - 0.107$	$4.1 \times 10^{-3} - 1.75 \times 10^{-2}$
DRE, %	11-9's – 9-9's	8-9's – 7-9's

Note: The pH of the liquid in a small sampling scrubber in the off-gas line remained basic throughout the test indicating essentially no HCl emission.

exhaust (Sample Location 2) for Runs 2A or 3A, and the DRE values reported for these two runs are based on the Sample 1 HCB values. The DREs for Runs 1 and 2A were greater than 10/9's (99.99999999) and 8/9's, respectively.

Run 2B was made at 75.8 lb/h HCB feed (approximately 30% of the total thermal load). Measurements for HCB showed 22.0 μg/m^3 at Sample Location 1 and less than 0.027 μg/m^3 at Sample Location 2. The molten salt bed temperature was held at 1685°F during the run. The DRE was >9/9's.

Run 3A was made at 112 lb/h HCB feed. An impinger measurement of less than 1.3 μg/m^3 in the vessel exhaust corresponded to a calculated DRE of greater than 8/9's.

Run 3B was the last run of the test series, and since results up to then were so promising, it was decided to test the molten salt unit with 100% HCB feed, i.e., no auxiliary fuel coke was used. A feed rate of 269 lb/h HCB was used to maintain the vessel at a temperature of 1805°F The HCB in the off-gas was 71 μg/m^3 downstream of the combustor and 0.16 μg/m^3 downstream of the baghouse. Note that this was the only run in which HCB was actually detected in the system's exhaust to the atmosphere. The 71 μg/m^3 and 0.16 μg/m^3 figures imply a baghouse removal efficiency of 99.77%. Post-test inspection of baghouse filters verified the presence of tears in the fabric.

Measured residual HCB in the molten salt overflow is shown in Table 3 for Tests 2B and 3B. The measured HCB concentration in the molten salt overflow was only 0.001 μg/g of melt in Test 2B but was 0.1 μg/g of melt in Test 3B. It may be that the last value was a result of contamination.

The salt dust from the baghouse contained <0.001 μg/g of dust; it could be recycled continuously back to the combustor if the HCB concentrations in the dust were of concern. Otherwise, this residual material would be disposed of as nonhazardous waste, as would the melt overflow.

TEST CONCLUSIONS

Bench-scale testing of HCB and chlordane was performed to optimize process parameters and verify analytical techniques to be utilized in pilot-scale tests which followed. For HCB destruction at a nominal salt bed temperature of 1839°F, a stoichiometry of 118%, and a residence time of 2-3/4 s, a destruction removal efficiency of >99.9999986% was achieved. Concentration of HCB in the off-gas and the salt bed, sampled during HCB feed, was <0.000017 ppmv and <0.00100 ppmw, respectively. For chlordane destruction, at a lower salt bed temperature of 1648°F and similar stoichiometry and residence time, a destruction removal efficiency of >99.999903% was achieved. Concentrations of chlordane in the off-gas and salt bed were <0.00267 ppmv and <0.0080 ppmv, respectively. Additionally, no chlorine or phosgene was detected within the analytical limits. HCl and NO_x were determined to be <100 ppm and <50 ppm, respectively. Monitoring, sampling, and analytical techniques to ensure conformance to EPA standards were verified. Additionally, a data base was established and subsequently verified for correlation of bench-scale and pilot-scale tests.

Pilot-scale tests of the same materials under similar process conditions produced similar or better destruction efficiencies. Typically, destruction efficiencies were >99.99999%. Improved performance characteristics in the pilot-scale units were attributed to greater salt inventory and greater residence times, the latter approaching 2 s. System limits were challenged by deliberate introduction of plant upset conditions. Stoichiometry was reduced to 0.78% from the nominal 120%; bed temperature was reduced over 115°F from the nominal operating temperature of 1830°F; superficial air velocity was increased from 2.0 fps to 2.7 fps; feed throughput was more than doubled; and auxiliary fuel was cut off in one case. None of these conditions resulted in off-gas emissions or POHCs in the spent melt which would be considered hazardous by RCRA criteria. Under these upset conditions, maximum concentrations of feed material in the combustor off-gas and spent melt was <0.0061 ppmw and <1.2 ppmw, respectively. Stack emissions were

<640 ppmv NO_x and <110 ppmv hydrocarbons. A small sampling scrubber in the off-gas remained basic throughout the test series, indicating essentially no HCl carryover.

In summary, these tests provided quantitative data on the performance of the Molten Salt Process in the destruction of hazardous waste. The data indicates more than adequate destruction efficiencies in accordance with RCRA criteria. These efficiencies were obtained with stack emissions and process spent melt residue characteristics well below minimum criteria for environmentally acceptable discharges. The data supports consideration of the Molten Salt Process as an environmentally acceptable alternative technology for the destruction of hazardous waste.

ENGINEERING STATUS

Reference Commercial System Design

Energy Systems Group has completed conceptual design of an MSD plant capable of 2000-lb/h throughput for liquid PCB. The plant is also capable of destroying other liquid and solid wastes. Design modifications may be needed on a case-by-case basis after evaluation of performance requirements. Figure 5 is a schematic of this plant and Figure 6 is an artist's concept.

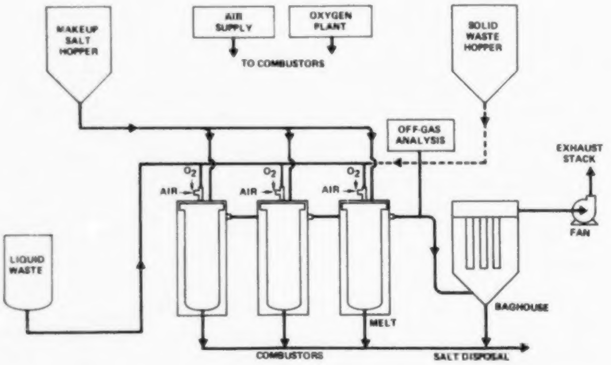

Figure 5. Simplified plant schematic.

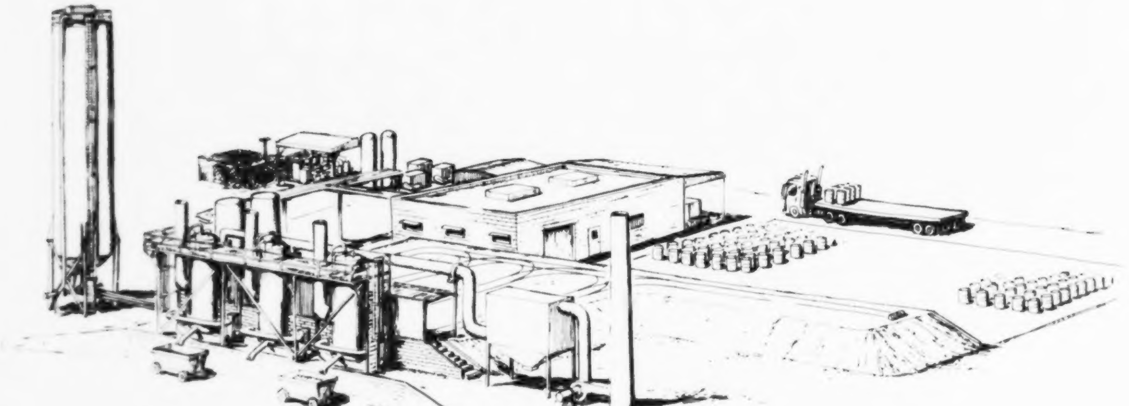

Figure 6. Molten salt destruction plant for hazardous wastes.

EVALUATION OF HAZARDOUS WASTE INCINERATION IN A DRY PROCESS CEMENT KILN

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ABSTRACT

This report presents the preliminary results of a test program conducted by SYSTECH Corporation at the Marquette Cement Plant in Oglesby, Illinois. The objective of this program was to compare the emissions resulting from co-firing low chlorine, high Btu liquid waste and coal in a dry process cement kiln with the emissions resulting from firing coal only.

The characteristics of the liquid waste burned during the test were examined by performance of standard analytical methods, with particular emphasis on organic composition. Destruction and removal efficiencies (DREs) were calculated for four principal organic hazardous constituents (POHCs) of the fuel: methylene chloride; methyl ethyl ketone; 1,1,1-trichloroethane; and toluene. Additional analyses were conducted on the stack gases to determine particulate loading, SO_2, NO_x, total gaseous nonmethane organics (TGNMO), HCl, and metals emissions. The kiln dust was also sampled and analyzed for metals and Extraction Procedure (EP) toxicity.

The results of these tests indicate that the cement kiln may be an ideal method of disposal for low chlorine, high Btu liquid wastes. The burning of liquid wastes in the kiln did not lead to any significant increase in particulate loading, SO_2, NO_x, TGNMO, or HCl over the levels observed during baseline coal-only test periods. Among the metals examined, only lead was found to significantly increase in emission rate during the liquid waste firing. No significant differences were observed in the EP toxicity of the kiln dusts sampled during the liquid waste and baseline tests, and only the concentration of lead was found to significantly increase in the kiln dust. Within the detection limits of the test method employed, the four POHCs measured were completely destroyed in the kiln.

INTRODUCTION

Marquette Company operates a cement plant in Oglesby, Illinois, which produces approximately 450,000 tons of cement yearly. Pulverized coal has been the primary fuel for this facility. Marquette proposes to construct and operate a liquid waste fuels resource recovery system at the Oglesby plant to facilitate the use of select combustible liquid waste materials such as high Btu (10,000 to 14,000 Btu/lb), low chlorine (2 to 5 percent) waste solvents as supplemental fuel in the kiln. The primary fuel will remain coal with an estimated 25 to 40 percent of the heat required by the manufacturing process supplied by the energy content of liquid waste materials. In order to assess the environmental effects of burning liquid wastes in the kiln, Marquette, in conjunction with the U.S. Environmental Protection Agency (EPA), the Illinois Environmental Protection Agency (IEPA), and SYSTECH Corporation performed a series of tests on the cement kiln at Oglesby on October 26 through 31, 1981.

The liquid waste fuels burned at the Oglesby facility were low chlorine, relatively high Btu waste solvents from ink and paint manufacturing and solvent recovery processes. Wastes of this type are classified as hazardous under the Resource Conservation and Recovery Act (RCRA) regulations primarily because of their ignitability, and have generally been considered unsuitable for recycling or reclaiming. Materials of this type have traditionally been disposed in landfill or incinerated without recovering their useful energy content. Incineration of such wastes in a cement kiln has the potential of minimizing any environmental damage from their disposal by destroying their combustibles while simultaneously recovering their useful energy content. Because of the high temperatures (2700° to 3000°F), long gas retention times (approaching 10 seconds), and high alkalinity in cement kilns, even highly toxic wastes such as PCBs have been demonstrated to be effectively destroyed. Earlier tests have demonstrated destruction and removal efficiencies (DREs) of such compounds exceeding 99.99 percent.[1,2]

The primary objective of the tests conducted in this program was to characterize the baseline emissions from the process when only coal was fired and to compare the results from this situation with those obtained when a combination of liquid waste and coal was being fired in the kiln. Specific emphasis was placed on characterizing the DREs of four principal organic hazardous constituents (POHCs) of the liquid wastes: methylene chloride; methyl ethyl ketone; 1,1,1-trichloroethane; and toluene. The experimental design and test methods used were developed to permit a comparison to be made between these two conditions rather than to accomplish a definitive environmental assessment of the burning of liquid wastes in a cement kiln. Therefore, it should be emphasized that the main purpose of this program was to determine whether co-firing liquid wastes increased the emissions over those normally observed during baseline conditions. The only statistically valid conclusions which can be derived from this test program fall into two categories: either the emissions were significantly increased or else no significant increase was observed. Although the mean values of the data collected may at first glance seem to indicate differences, only by considering the numbers of samples taken and the calculated sample standard deviations can statistically valid conclusions be reached. This summary report focuses on system emissions while the final EPA report will include information regarding any effects that the liquid waste may have had on the characteristics of the cement product. These effects are expected to be negligible and should not impact the environmental considerations regarding this project.

METHODS

The test program conducted at the Oglesby facility was designed to collect 2 days of samples and data during both the baseline and liquid waste burns. Because of difficulties encountered in receiving and delivering a sufficient quantity of liquid waste and periodic unscheduled kiln down times, however, only 1 day of testing was accomplished with liquid waste and only 1 1/2 days during baseline conditions.

Figure 1 shows a schematic flow diagram of the dry process cement kiln tested at Oglesby. Samples and data were collected from the sites labeled A through E. Liquid waste was pumped from a storage tanker into the flame of the kiln through a specially designed delivery nozzle.

The liquid waste burned in the test program was sampled at Site A and analyzed for heating value, chlorine, sulfur, nitrogen, and water content by standard ASTM reference methods. Method 8.01 (SW 846 Test Methods for Evaluating Solid Waste: Physical/Chemical Methods) was employed to identify the concentrations of methylene chloride; methyl ethyl ketone; 1,1,1-trichloroethane; and toluene. Other organics were qualitatively identified by a general scanning procedure employing gas chromatography with flame ionization detection (FID). Metals were identified by inductively coupled plasma emission spectroscopy (ICP). Atomic absorption spectroscopy (AA) was employed for mercury analysis.

Stack emissions were sampled at Site C and examined for total gaseous nonmethane organics (TGNMO) by EPA Method 25. Integrated bag samples of stack gases were analyzed by gas chromatography with FID according to EPA Method 23 for methylene chloride; methyl ethyl ketone; 1,1,1-trichloroethane; and toluene (see Federal Register, June 11, 1980, and EPA 600/4-80-003). Particulate emissions were measured by EPA Method 5, and SO_2 was measured by a modified EPA Method 8 procedure employing 3 percent H_2O_2 in the impingers to collect SO_2 and sulfuric acid mist. Metals emissions were determined from an analysis of the Method 5 filters and the acetone probe rinses by ICP spectroscopy. Mercury emissions were determined by AA spectroscopy. Emission of nitrogen oxides was determined by EPA Method 7. A midget impinger train containing sodium hydroxide was used to collect hydrochloric acid emissions. Analysis of the impinger contents was accomplished by a mercuric nitrate titration.

The kiln dust collected at Site D from the last two banks of the electrostatic precipitator (ESP) was analyzed for metals by ICP spectroscopy. Mercury was analyzed by AA spectroscopy. The potential for leaching of metals from this dust was assessed by conducting EP toxicity tests.

RESULTS AND DISCUSSION

Figure 2 illustrates the testing and process operating log for the test period. It is evident that the kiln experienced several periods of down time during the tests. Three tests, designated Test Nos. 1, 2, and 3, were conducted during the liquid waste burns on October 28, 1981. Test Nos. 4, 5, and 6 were conducted during baseline burns on October 30 and 31, 1981. Each test consisted of approximately 2 hours during which samples and data were collected.

The liquid waste used for this test was typical of that which would be specified for a permanent facility operation. The liquid waste was sampled every hour during the test period, and composites were made of the hourly samples to represent the material fired during each of the three co-firing conditions. The results of these analyses are presented in Table 1. The liquid waste had a mean heating value of 12,350 Btu/lb and a mean chloride content of 4.54 percent. The primary metallic constituent of the waste was lead, with a mean concentration of 1,800 ppm. No PCBs were detected in the waste and the POHCs designated for these tests comprised an average of 24.7 percent of the liquid waste. The other organic constituents listed in Table 1 were qualitatively identified by retention time in the GC analysis.

It is anticipated that in normal operation a substitution rate of 25 to 40 percent liquid waste would be used; however, during the test period a limitation on the quantity of liquid waste available precluded firing the waste at these rates. The substitution rates for the liquid waste expressed as a percent of the total heat input of the combined coal and liquid waste stream were 14.0 percent for Test No. 1, 11.2 percent for Test No. 2, and 12.8 percent for Test No. 3.

Stack emissions measured during the test program are shown in Table 2. None of the POHCs measured were detected in the stack gas samples during either co-firing or coal-only combustion. Table 3 shows the DREs of the kiln for the POHCs measured during the liquid waste tests. Since none of the POHCs were detected at the minimum detection limit of the test method (nominally 0.1 ppm), the DREs expressed can be considered minimum values. The efficiency of combustion of organic compounds is also supported by the results of the Method 25 tests which show no significant increase at a 95 percent confidence level in TGNMO emissions during co-firing when compared with baseline results. These results indicate that there is no measurable contribution to the hydrocarbon emissions from the stack due to the addition of liquid waste to the kiln.

In addition to hydrocarbons, Table 2 also presents the particulate, SO_2, NO_x, and HCl emissions under the co-firing condition for Test Nos. 1, 2, and 3 versus the coal condition during Test Nos. 4, 5, and 6. Although unstable operating conditions contributed considerable variability within the data sets, there was no significant increase at a 95 percent confidence level over baseline conditions in particulate, SO_2, NO_x, or HCl emissions while cofiring liquid waste.

Table 4 shows the results of metals analyses of stack particulates sampled during this test. A slight increase in lead emissions over baseline conditions (from .04 to .072 lb/hr) was observed during the co-firing tests. Other metals examined did not increase significantly at a 95 percent confidence level with the burning of the liquid wastes. Table 4 also shows the results of metals analyses of the kiln dust sampled during this test. An increase in the lead concentration in the kiln dust was observed during the liquid waste firing. This increase was from approximately .02 percent during coal-only conditions to .05 percent during the co-firing conditions. The other metals present in the liquid waste were not observed to significantly increase in concentration at a 95 percent confidence level in the kiln dust when the liquid waste was co-fired in the kiln. Further, the leachability of metals from the kiln dust did not increase significantly and remained orders of magnitude below the allowable limits specified by the EPA.

The inclusion of metals in the liquid waste burned in the cement kiln appears to have had a minimal impact on the discharge of metals from the stack or on the amount occurring in the kiln dust. This may indicate that many metals are deposited in the cement clinker and become incorporated in the crystalline structure of the cement product.

CONCLUSIONS

The general conclusion that can be drawn from this test program regarding the the environmental impacts of firing liquid wastes in a cement kiln is that the liquid waste does not significantly increase the emissions of particles, hydrocarbons, SO_2, NO_x, or HCl from the stack. Within the detection limits of the test methods employed, the four POHCs examined were completely destroyed in the kiln. A slight increase in lead in the particulate and kiln dust was observed, but other metals examined did not show a significant increase either in stack emission or in the process collected kiln dust with the burning of the liquid waste. The kiln dust was determined by the EP toxicity test to be nonhazardous and could be landfilled even when liquid wastes are cofired. In general, the use of liquid waste in this test produced only minor changes in the emissions from the kiln and revealed that the kiln may provide a promising waste disposal method for high Btu, low chlorine wastes.

REFERENCES

1. Ahling, B., "Combustion Test with Chlorinated Hydrocarbons in a Cement Kiln at Stora Vika Test Center," Swedish Water and Air Pollution Research Institute, Stockholm, March 16, 1978.

2. Knut Trovaag, "Hazardous Waste Incineration in a Cement Kiln," International NATO/CCMS Hazardous Waste Symposium, October 5, 1981.

TABLE 1. WASTE FUEL ANALYSIS

	Test 1	Test 2	Test 3
Heat content (Btu/lb)	12,210	13,012	11,823
Ash (%)*	12.13	7.82	6.85
Chloride (%)	3.56	4.28	5.80
Sulfur (%)	.09	.09	.06
Nitrogen (%)	.13	.10	.20
Water (%)	10.70	10.3	11.80
Metals (ppm)			
Cadmium	3	2	1
Chromium	725	565	446
Copper	195	167	177
Lead	2520	1820	1050
Manganese	47	35	42
Mercury	.076	.104	<.032
Nickel	52	42	107
Zinc	1770	1290	905
Quantified organics (%)	23.88	22.01	28.26
Methylene chloride	2.72	2.94	6.27
1,1,1-trichloroethane	1.86	1.63	1.97
Methyl ethyl ketone	7.51	8.90	8.18
Toluene	11.79	8.54	11.84
PCBs†	N.D.	N.D.	N.D.
Other organics (%)§	53.29	59.87	53.09
Methanol			
Ethanol			
2-Propanol			
Acetone			
Methyl acetate			
Ethylene chloride			
2-ethoxy-ethyl acetate			
Methyl isobutyl ketone			
Butyl acetate			
4-hydroxy-4-methyl-2-pentanone			
Benzene			
Ethyl benzene			
Styrene			
C_9 Alkyl benzenes			
Paraffins (C_6-C_{12})			
Xylene			
Unidentified (2 compounds)			

* All (%) are weight percent.

† None detected at a detection limit of .005 percent.

§ Weight percent of other organics = 100 percent - ash - water - quantified organics. Compounds listed in this category were not quantified.

TABLE 2. OGLESBY EMISSION TEST RESULTS

Run No.	Percent substitution of heat input by liquid wastes	Hydrocarbons POHCs*	Hydrocarbons TGNMO† ppm C	Part. gr/scf	Part. lb/hr	SO_2 ppm	SO_2 lb/hr	NOx ppm	NOx lb/hr	HCl ppm	HCl lb/hr
Liquid waste co-firing											
1	14	N.D.§	220	0.125	63.8	41	25.3	388	162.5	405	137
2	11.2	N.D.	800	0.101	58.7	8	5.3	590	280.4	232	89
3	12.8	N.D.	390	0.086	52.7	5	3.9	653	328.0	289	119
Coal-only											
4	---	N.D.	1350	0.075	42.9	42	27.7	864	402.9	522	196
5	---	N.D.	670	0.099	50.1	69	40.5	846	350.2	435	145
6	---	N.D.	1740	0.105	55.7	168	103.2	1052	458.7	654	230

* POHCs tested for were: methylene chloride; toluene; methyl ethyl ketone; and 1,1,1-trichloroethane.

† Method 25 hydrocarbons expressed as ppm carbon.

§ None detected at a nominal detection limit of 0.1 ppm.

TABLE 3. DREs CALCULATED FOR THE CO-FIRING TESTS

	Minimum DREs*			
Test numbers	Methylene chloride	Methyl ethyl ketone	1,1,1-trichloroethane	Toluene
1	99.869	99.960	99.718	99.968
2	99.851	99.959	99.604	99.947
3	99.917	99.961	99.710	99.968
Average	99.879	99.960	99.677	99.961

* The DREs indicated have been adjusted by a sensitivity analysis approach to include the impact of random measurement errors on the DRE calculations. The stated values therefore actually represent the minimum DREs observable in the cement kiln by employing the test methods described in this report.

TABLE 4. METALS TEST RESULTS

Kiln Dust Analysis (ppm)

Element	Run No.	Liquid waste 1	Liquid waste 2	Liquid waste 3	Avg.	Coal only 4	Coal only 5	Coal only 6	Avg.
Cd		18	16	15	16	19	22	30	24
Cr		23	24	31	26	23	28	24	25
Cu		26	24	25	25	24	30	30	28
Pb		524	511	488	507	173	186	167	175
Mn		632	656	795	694	681	759	655	698
Ni		25	31	31	29	22	27	29	26
Hg		.22	.30	.40	.31	.40	.22	.26	.29
Zn		71	66	70	69	49	57	75	60

Kiln Dust EP Toxicity Test Results (mg/ℓ)

	Run No.	Liquid waste 1	Liquid waste 2	Liquid waste 3	Avg.	Coal only 4	Coal only 5	Coal only 6	Avg.
As		<.003	<.003	<.003	<.003	.006	.004	.003	<.005
Ba		.593	1.020	.685	.766	.753	.649	1.020	.807
Cd		.004	.481	<.003	.167	.073	.017	.897	.329
Cr		<.020	.088	.032	.047	<.020	.020	.035	.025
Pb		<.043	.919	<.043	.335	<.043	<.043	.713	.266
Hg		<.0008	<.0008	<.0008	<.0003	<.0008	<.0008	<.0008	<.0008
Se		.215	.343	.179	.246	.350	.414	.502	.422
Ag		<.007	<.007	<.007	<.007	<.007	.013	<.007	<.009

Metals Emissions On Particulates (lb/hr)

	Run No.	Liquid waste 1	Liquid waste 2	Liquid waste 3	Avg.	Coal only 4	Coal only 5	Coal only 6	Avg.
Cd		.003	.001	.001	.002	.002	.003	.002	.002
Cr		.075	.030	.054	.053	.020	--	--	.020
Cu		--	--	--	--	--	--	--	--
Pb		.105	.060	.052	.072	.042	.036	.043	.040
Mn		.007	.004	.003	.005	.003	.002	.003	.003
Hg		.0002	.0002	.0001	.002	.0003	.0003	.0003	.003
Ni		.160	.061	.065	.095	.044	.018	.032	.031
Zn		.049	.005	.001	.018	.002	.002	--	.002

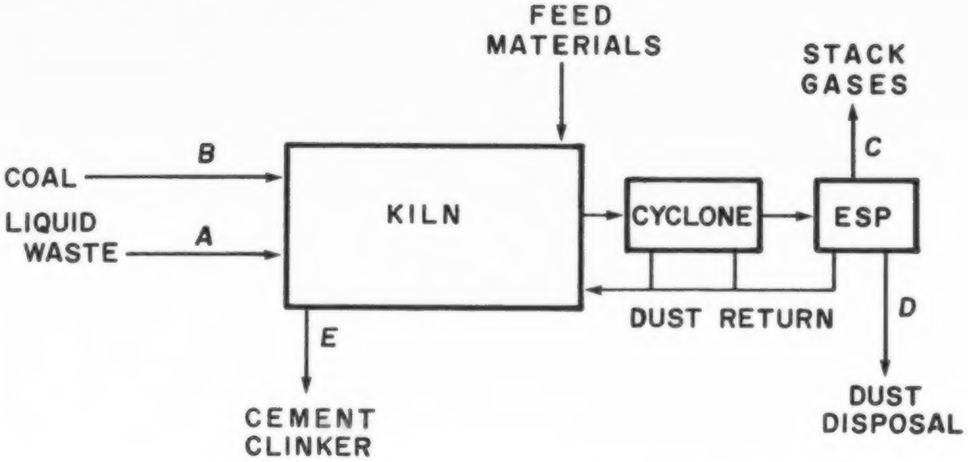

Figure 1. Marquette-Oglesby cement kiln schematic.

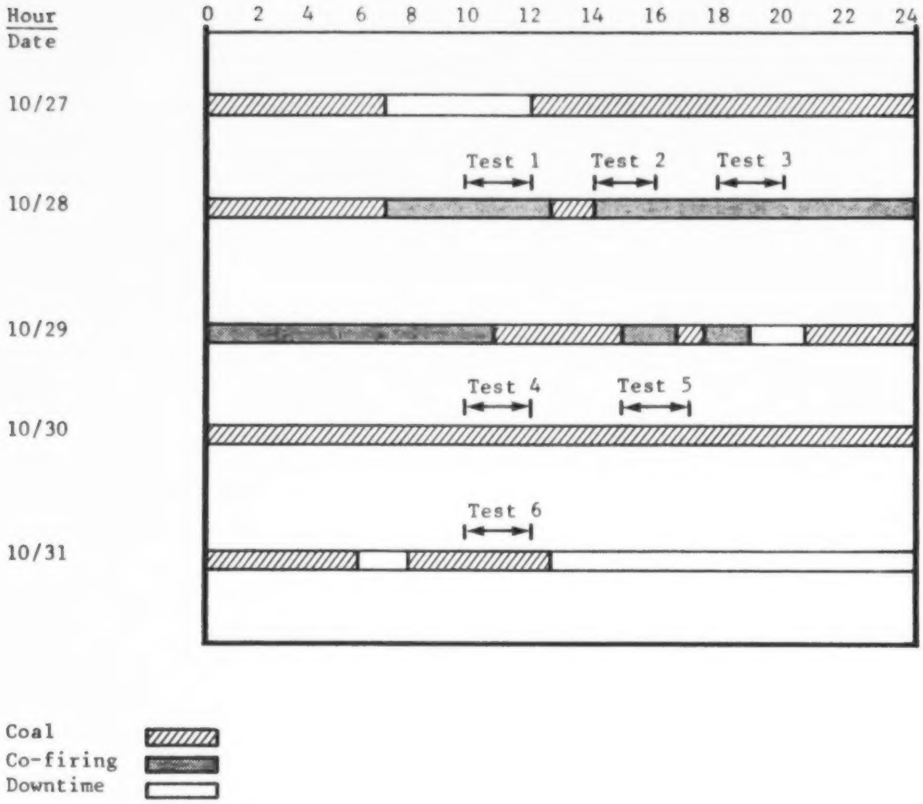

Figure 2. Process operations log.

* U.S. GOVERNMENT PRINTING OFFICE 1983 -659-095/1930